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LXXXVII. *An Empirical Law of Atomic Repulsion in Relation to the Cohesional Properties of Solids.* By G. A. TOMLINSON, B.Sc.*

PART I.

(1) **T**HE conception that the atoms of a solid are in equilibrium under opposing forces of attraction and repulsion helps us considerably to, at least, a partial comprehension of many of the properties of solids, such as solidity itself or permanence of form, elasticity, some features of the lattice structure, atomic vibration phenomena, and the energy of combination of atoms. Recently the writer has suggested theories to account for solid friction⁽¹⁾ and elastic hysteresis⁽²⁾ based on this conception. It is of interest to remark that most lines of thought lead to the conclusion that the repulsion is a very abrupt force with a considerably higher gradient than the attraction, which itself varies very rapidly with the distance between the atoms.

It is probably safe to say that in general we know more about the nature of the attraction than of the repulsion. Indeed, all attempts that have been made to explain the latter have admittedly been little more than surmises, and in this paper the question of the nature of the repulsion is only touched upon where necessary. The paper is rather an

* Communicated by Sir J. E. Petavel.

attempt to ascertain what properties may be ascribed to the repulsion as inferred from known perceivable properties of matter.

(2) Certain of the more obvious properties will first be discussed briefly. The repulsion is universal throughout the elements, otherwise groups of atoms would coalesce under cohesive attraction. The repulsion must be a static effect, although a number of earlier physicists, notably Sutherland⁽³⁾, have developed theories of the solid state in which the cohesive force between atoms is supposed to be in equilibrium with a kinetic repulsion. Two simple considerations, however, go to prove the existence of a static force. The kinetic theory of repulsion, which doubtless plays some part in the atomic equilibrium, must itself ultimately admit of the existence of a powerful static repulsion acting during the instant of collision to reverse the momentum of the moving atoms. Further, we know that the stability of the atoms, as perceived by the elastic behaviour of the solid, tends to become greater as the temperature is reduced, even down to the region of absolute zero at which any kinetic repulsion must vanish.

The magnitude to which the repulsion may attain appears to be unlimited, at least within the limits of experimental resources. It is known that the equilibrium force between atoms, commonly called the intrinsic pressure, is large compared with any pressure we can apply to matter as a whole. Thus, for example, in the case of polar compounds of the KCl type, the force of attraction, and therefore of repulsion, between the ions is of the order 10^{-4} dyne, which corresponds to a pressure of about 10^{11} dynes per sq. cm., or about 100,000 atmospheres. It is probable that this large force of repulsion is exceeded by the repulsions acting in gaseous atomic collisions at high temperatures. If we consider the energy of a gas molecule in a flame, for example, assuming the temperature to be about 2000° Abs., the energy possessed by the molecule is about 4×10^{13} ergs. It has been shown by Born⁽⁴⁾ that the potential energy of each atom in the KCl type of lattice, associated with the repulsion force, is of the order 0.7×10^{-14} ergs. Thus the potential energy of repulsion in the course of the gaseous molecular collision must be about fifty-seven times the latter amount, and must involve a correspondingly greater force of repulsion. Exactly how much greater it is difficult to say *, but the example indicates

* Later in the paper it is shown to be probable that the potential energy of repulsion is proportional to the force of repulsion in the solid state, but one is not justified in extrapolating such a relation so far as to include the case of the gaseous atom.

that values of the repulsion do actually occur which are far greater than we can produce by pressure.

It seems clear from this that no upper limit can be assigned to the repulsion or to the corresponding distance between the atom centres. The lower limit to the repulsion, on the other hand, is of course zero, and it is of interest to inquire if there is any way of estimating what displacement of the atoms is required for the repulsion to vanish. If it is granted that the stability which is characteristic of the solid state is due to the action of the static repulsion, some clue as to the range of the repulsion can be obtained. It is known that the total dilatation of most of the elements at the melting-point is roughly constant and of the order 1 or 2 per cent. On changing to the liquid state a further dilatation of about the same amount occurs. The total expansion of the lattice throughout the range of the solid state is thus approximately 3 per cent., from which it is probable that the effective lower part of the range of the repulsion is only of the order 0.03 of the distance between the atoms.

(3) The next feature of the repulsion to be considered is the variation of the force with relative displacement of the atoms. The most important work done in this field is that of Born⁽⁴⁾, Landé, and a group of other mathematical physicists in Germany. Born deals with those of the alkali halides in which the atoms are known to lie on a simple interlaced cubic lattice, and he is on comparatively safe ground as regards the attraction between the atoms, which is regarded as a simple Coulomb attraction between the positive and negative ions. This assumption has been corroborated fairly well by Slater⁽⁵⁾ from his own determinations of the compressibilities of the various salts. Briefly, Born takes the potential energy of a unit cube of the lattice to be

$$\phi = -\frac{a}{\delta} + \frac{b}{\delta^m}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

δ being the dimension of the elementary cube.

The second term is an assumption, and implies that the repulsion can be represented by an inverse function of the distance between the atom centres

$$R \propto \frac{1}{\delta^{m+1}}.$$

The theoretical compressibility can be calculated from the potential energy equation, and Born finds that if $m+1$ is

taken to be about 10, a fairly good agreement with observed compressibilities is obtained throughout the series of salts.

It appears to the writer that some further information as to the character of the repulsion can be derived by adopting a somewhat different procedure, as follows:—The most accurate determinations of the compressibilities of the alkali halides are probably those made quite recently by Slater⁽⁶⁾, who also made reliable observations of the change of compressibility with pressure up to 12,000 atmospheres. If K is the compressibility at a pressure P , it was found by Slater that

$$K = K_0(1 - \lambda P), \quad (2)$$

where K_0 is the compressibility under zero pressure and λ is a constant.

Let us consider any salt having the NaCl cubic lattice with a distance r_0 between neighbouring positive and negative ions when under zero pressure. When an external pressure P is applied let the ions be forced together by a small amount z . The external force due to the pressure acting on any one atom is

$$F = P(r_0 - z)^2. \quad (3)$$

The relation between P and z can be found from equation (2). Considering a quantity of the substance having a volume V_0 at zero pressure, compressed to a volume V by the pressure P , we have

$$V = V_0 \frac{(r_0 - z)^3}{r_0^3}$$

and

$$\begin{aligned} K &= K_0(1 - \lambda P) = -\frac{1}{V} \frac{dV}{dP} \\ &= \frac{3}{(r_0 - z)} \frac{dz}{dP}. \end{aligned}$$

Hence

$$\begin{aligned} K_0 \int_0^P (1 - \lambda P) dP &= 3 \int_0^z \frac{dz}{(r_0 - z)}, \\ K_0(P - \frac{1}{2}\lambda P^2) &= -3 \log \frac{(r_0 - z)}{r_0} \\ &= \frac{3z}{r_0} + \frac{3z^2}{2r_0^2} + \dots, \quad . . . (4) \end{aligned}$$

expanding as far as the second power of $\frac{z}{r_0}$. The last equation leads to

$$\lambda P = 1 \pm \sqrt{1 - \frac{6\lambda z}{r_0 K_0} - \frac{6\lambda z^2}{2r_0^2 K_0}}. \quad . . . (5)$$

In this the term $\frac{6\lambda z}{r_0 K_0}$ is well below unity for the highest pressure used by Slater, and the term $\frac{6\lambda z^2}{2r_0^2 K_0}$ is still smaller.

The square root can therefore be expanded, giving

$$\lambda P = 1 \pm \left(1 - \frac{3\lambda z}{r_0 K_0} - \frac{36\lambda^2 z^2}{8r_0^2 K_0^2} - \frac{3\lambda z^2}{2r_0^2 K_0} \dots \right).$$

Only one of the two solutions is possible, giving P in terms of z ,

$$P = \frac{3z}{r_0 K_0} + \frac{36\lambda z^2}{8r_0^2 K_0^2} + \frac{3z^2}{2r_0^2 K_0} \dots \quad (6)$$

If A and R denote the attraction and repulsion on any atom along any of three directions of the lattice, we have for equilibrium

$$A - R + F = 0. \dots \dots \quad (7)$$

The potential energy of the lattice has been calculated by Madelung⁽⁷⁾, who finds the total energy of a single ion in a complete lattice to be

$$U = -\frac{1.742 e^2}{r_0}, \dots \dots \quad (8)$$

where e is the electron charge.

This energy is equally distributed with respect to the three axes of the lattice, and the energy $\frac{U}{3}$ is equally divided as regards the two directions along the axis with the ion as origin. Hence the attraction of the whole lattice on any one ion in any one direction is given by

$$\frac{1}{6} \frac{dU}{dr} = \frac{1.742}{6} \frac{e^2}{r_0^2},$$

and, on the assumption that the repulsion is a force exerted only by immediate neighbours in the lattice, equation (7) can be written in the form

$$R = \frac{1.742}{6} \frac{e^2}{(r_0 - z)^2} + (r_0 - z)^2 \left[\frac{3z}{r_0 K_0} + \frac{36\lambda z^2}{8r_0^2 K_0^2} + \frac{3z^2}{2r_0^2 K_0} \right], \dots \quad (9)$$

using the results of equations (3) and (6).

If we denote by β the number $\frac{1.742}{6}$, and expand and rearrange, this becomes

$$R = \frac{\beta e^2}{r_0^2} + \left(\frac{2\beta e^2}{r_0^3} + \frac{3r_0}{K_0} \right) z + \left(\frac{3\beta e^2}{r_0^4} + \frac{9\lambda}{2K_0^2} - \frac{9}{2K_0} \right) z^2 + \dots$$

$$= L + Mz + Nz^2 + \dots \quad (10)$$

According to this equation the repulsion can be expressed as a simple power series in z , the displacement of the atom from the normal equilibrium position. All the constants concerned in the coefficients are known and have the values which are given numerically in Table I.

We may observe that all the coefficients are positive as far as the expansion has been taken. One is hardly justified in including any further terms in the series of equation (10), since it is not known how far Slater's observed relation $K = K_0(1 - \lambda P)$ may hold for still higher pressures than he used. Any modification of this relation, such as the inclusion of a term in P^2 for example, which might be found necessary could higher pressures be employed might materially affect the coefficient of z^2 and the higher powers of z in equation (10). Although the compressibility observations were carried up to 12,000 atmospheres, they actually cover only a small part of the range of the repulsion. This can be readily seen by putting numerical values into the equations. Thus from equation (4) it is found for KCl, for example, that at 12,000 atmospheres z has a value $0.019 r_0$ or 0.0595×10^{-8} . Using this value in equation (10), we have for the repulsion

$$R = 0.675 \times 10^{-4} + 2.10 \times 10^4 + 0.0595 \times 10^{-8}$$

$$+ 3.16 \times 10^{12} \times 0.0595^2 \times 10^{-16}$$

$$= 0.675 \times 10^{-4} + 0.125 \times 10^{-4} + 0.011 \times 10^{-4}$$

$$= 0.81 \times 10^{-4}.$$

The repulsion is therefore only increased by about 18 per cent. above its intrinsic equilibrium value given by the first term. The numerical case further shows clearly that terms beyond z^2 are not needed within the range covered by experimental data.

It is of interest to observe from equation (10) that the value of $\frac{dR}{dz}$ for $z=0$ is given by

$$\frac{2\beta e^2}{r_0^3} + \frac{3r_0}{K_0},$$

TOMLINSON.]

[To face page 1014.

TABLE I.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.
Salt.	r_0 .	K_0 .	λ .	$\frac{2\beta e^2}{r_0^3}$.	$\frac{3r_0}{K_0}$.	$\frac{3\beta e^2}{r_0^4}$.	$\frac{9\lambda}{2K_0^2}$.	$\frac{9}{2K_0}$.	$\frac{\beta e^2}{r_0^2} = L$.	M.	N.	$\frac{M}{L} = p$.	$p = \sqrt{\frac{2N}{L}}$.
LiF	2.07×10^{-8}	1.53×10^{-12}	11.7×10^{-12}	1.49×10^4	4.05×10^4	1.08×10^{12}	22.4×10^{12}	2.95×10^{12}	1.54×10^{-4}	5.54×10^4	20.53×10^{12}	3.59×10^8	5.16×10
LiCl	2.57	3.41	19.8	0.777	2.26	0.455	7.65	1.32	1.00	3.04	6.78	3.04	3.68
LiBr	2.74	4.31	24.5	0.642	1.90	0.353	5.95	1.04	0.880	2.54	5.26	2.88	3.45
NaCl	2.815	4.20	21.9	0.591	2.01	0.315	5.60	1.07	0.833	2.60	4.84	3.12	3.40
NaBr	2.97	5.08	25.5	0.505	1.75	0.255	4.45	0.89	0.750	2.25	3.81	3.00	3.18
KF	2.665	3.31	20.1	0.698	2.42	0.393	8.26	1.36	0.930	3.12	7.29	3.36	3.96
KCl	3.13	5.63	26.5	0.430	1.67	0.200	3.76	0.80	0.675	2.10	3.16	3.11	3.06
KBr	3.29	6.70	31.8	0.371	1.47	0.169	3.19	0.67	0.610	1.84	2.69	3.02	2.97
KI	3.525	8.54	39.1	0.302	1.24	0.128	2.41	0.53	0.531	1.54	2.01	2.90	2.75
RbBr	3.42	7.94	35	0.330	1.29	0.145	2.50	0.56	0.565	1.62	2.08	2.87	2.71
RbI	3.66	9.58	43	0.269	1.14	0.110	2.11	0.47	0.492	1.41	1.75	2.87	2.67

whereas the value of $\frac{dA}{dz}$ for $r=r_0$ is $\frac{2\beta e^2}{r_0^3}$. Hence $\frac{dR}{dz}$, the repulsion gradient, must exceed the attraction gradient, and columns 5 and 6 show that $\frac{dR}{dz}$ is actually about four to five times as great as $\frac{dA}{dr}$.

(4) Let us next give attention to a particular correlation which exists amongst the coefficients of equation (10) for the various salts. In the first place, for each individual salt the coefficients L, M, and N are fairly closely related in such a way that

$$\begin{aligned} M &= pL \\ \text{and} \\ N &= \frac{1}{2}pM = \frac{1}{2}p^2L. \end{aligned}$$

Further, throughout the series of salts, as shown by column 13, the value of p is nearly constant and about equal to 3×10^8 . The two fluorides tend to exhibit values somewhat higher than the rest of the salts. Thus for each salt the repulsion can be expressed as

$$R = L(1 + pz + \frac{1}{2}p^2z^2 + \dots), \quad \dots \quad (11)$$

which is the expansion as far as the second power of the exponential relation

$$R = Le^{pz}, \quad \dots \quad (12)$$

in which L is the intrinsic repulsion under no pressure.

Certain small discrepancies occur as regards the second coefficient N, which are shown by column 14, giving the

values of p computed from $p^2 = \frac{2N}{L}$ alongside the values obtained from $p = \frac{M}{L}$. The two values can, however, be

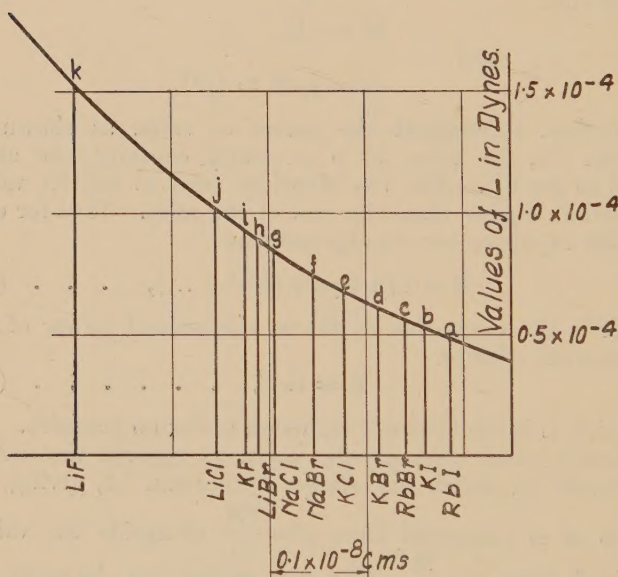
regarded as in reasonable agreement as regards order of magnitude, as it must be realized that the coefficient of z^2 in equation (10) is subject to some uncertainty arising from the natural limitations of the experimental data available. This can be seen by observing that the principal term in N is

$\frac{36\lambda}{8K_0^2}$, a term involving λ , which naturally cannot be as well

determined as K_0 . The coefficient M, which contains only K_0 as an experimental constant, is more certain, and the values of p consequently approach more closely to a constant value averaging about 3×10^8 .

Since we find a similar relation between the coefficients for every one of the salts of the series, we must regard it as strongly suggestive that the repulsion is an exponential function of z . Such a view receives distinct further support from the fact that p has nearly the same value for all the salts. This means that the various short portions of the repulsion range which have been explored by means of compressibility data for the different salts all tend to form portions of one common exponential curve, and may be depicted as in fig. 1. In this diagram the ordinates at the points $a, b, c,$

Fig. 1.



etc. represent the intrinsic repulsion under zero pressure, that is, the coefficient L for the various salts RbI , RbBr , KI , etc. The variation in R , caused by pressures up to 12,000 atmospheres, is represented by a small part of the complete exponential curve extending upwards for a short distance from each point a, b , etc.

(5) A brief discussion of the above results at this stage may not be out of place. It may be remarked, to begin with, that our conclusions are based almost entirely upon experiment. It is true that it has been assumed that the attraction

of the atoms is a direct electrostatic force between the valency electrons, but there is so much different evidence in support of this that it may be regarded as a fairly safe assumption. Hence, granted the validity of this assumption, the exponential character of the repulsion is an empirical deduction from the observed changes of volume with pressure. Two possible properties of the repulsion are suggested by the above exponential expression. One is that the force is a function of the closeness of the atom "boundaries" rather than a function of the distance between the atom centres, and that it is more in the nature of a quasi-elastic resistance to approach or to interpenetration than a central force corresponding to an inverse power law of force. The other property is that, for the groups of atoms involved in this series of salts, the force is independent of the nature of the atom. The constant L is determined solely by the atomic distance, and, since p is found to have approximately the same value throughout, the expression for R is therefore

TABLE II.

	r_0 .	$\frac{\beta e^2}{r_0^2} = L$.	$\frac{23e^2}{r_0^3}$.	$\frac{3r_0}{K_0}$.	M .	$\frac{M}{L} = p$.
AgCl ...	2.77×10^{-8}	0.86×10^{-4}	0.62×10^4	3.47×10^4	4.09×10^4	4.76×10
AgBr ...	2.89	0.79	0.55	3.21	3.76	4.76

independent of the constituent atoms of the salt. As regards both these properties it is significant that the atoms concerned form the members of two well-defined groups of the periodic system. Each group is characterized by a similar outer shell of electrons which perform the function of defining the boundary of the atom. The second property is therefore quite consistent with the first, on the view that the repulsion is a resistance to the interpenetration of the atom boundaries.

There is reason for thinking that a repulsion having a different constant p is found on passing to another group of the periodic system. Thus the two silver salts AgCl and AgBr, although having the same type of lattice as the alkali halides, have compressibilities 2.4×10^{-12} and 2.7×10^{-12} respectively, values which lead to the coefficients in Table II.

There are not sufficient data to determine the third coefficient N for these salts, and one is not justified in drawing any firm conclusions from the behaviour of only two salts; but as far as these results go we again have a constant value

for p , but a value considerably different from that previously found for the alkali group of metals.

If the repulsion is an exponential function, this itself would lead us to believe that the repulsion is very different in nature from the simple Coulomb attraction. In fact, in attempting to form any mental picture of the physical cause of a force obeying such a law it seems necessary to surmise that some complex statistical process intervenes between the repulsion as perceived and the fundamental electric forces concerned. One may mention certain other evidence tending to show that the attraction and repulsion are quite distinct phenomena. Thus there are elements such as helium, neon, etc. which exhibit, as far as we know, almost no attraction at all, either for another like atom or for a different atom, as shown by the extremely low boiling-point and by the chemical inertness of these substances. Yet these atoms behave just as other gaseous atoms in exerting powerful repulsion during collision, showing that this force can be exerted independently of the existence of an attraction.

If the repulsion follows the exponential law suggested,

$$R = L\epsilon^{pz},$$

it follows that the potential energy associated with a repulsion R is

$$E_r = \frac{L}{p}\epsilon^{pz} = \frac{R}{p},$$

or the potential energy is proportional to the repulsion.

The energy associated with an attraction A is given by

$$E_a = \frac{\beta e^2}{r}.$$

Under zero pressure

$$E_r = \frac{L}{p} = \frac{\beta e^2}{r_0^2 p},$$

$$E_r = \frac{1}{pr_0} E_a. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

For the salts previously considered r_0 has an average value of about 3×10^{-8} and p is about 3×10^8 ; hence the repulsion potential energy is approximately one-ninth of the attraction energy. This is of interest, because it is in agreement with the conclusions of Born and Landé.

(6) An expression can be derived from the exponential relation for the repulsion, giving the compressibility.

We have

$$R = L\epsilon^{pz},$$

$$\left(\frac{dR}{dz}\right)_{z=0} = pL = p\frac{\beta e^2}{r_0^2},$$

and from equation (10)

$$\left(\frac{dR}{dz}\right)_{z=0} = \frac{2\beta e^2}{r_0^3} + \frac{3r_0}{K_0}.$$

Hence

$$\begin{aligned} \frac{1}{K_0} &= \frac{\beta e^2}{3} \left(\frac{p}{r_0^3} - \frac{2}{r_0^4} \right) \\ &= \frac{\beta e^2}{3} \frac{pr_0 - 2}{r_0^4}. \quad . \quad . \quad . \quad . \quad (14) \end{aligned}$$

TABLE III.

Salt.	pr_0 or n .
LiF	7.45
LiCl	7.85
LiBr	7.95
NaCl	8.8
NaBr	9.0
KF	8.9
KCl	9.77
KBr	9.95
KI	10.22
RbBr	9.85
RbI	10.5

This may be compared with the formula derived by Born and Landé⁽⁴⁾, which in the notation of this paper may be written

$$\frac{1}{K_0} = \frac{\beta e^2}{3} \frac{(n-2)}{r_0^4}, \quad . \quad . \quad . \quad . \quad (15)$$

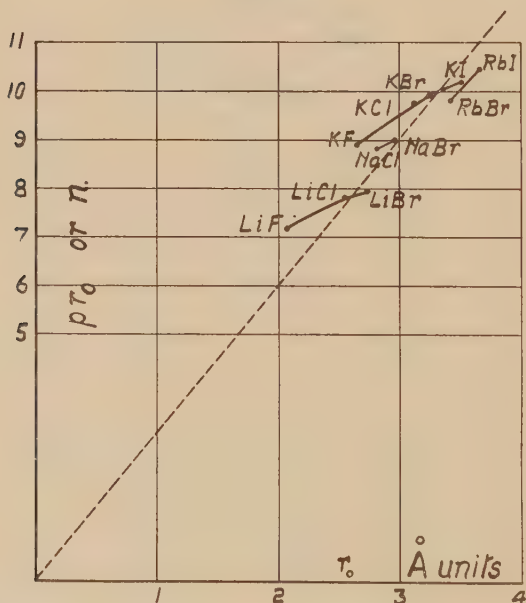
where n is the exponent in their assumed inverse power law of repulsion, and is considered to have a value about 10.

It is interesting to notice that these expressions are identical, except that in (14) pr_0 takes the place of Born's exponent n .

The comparison between the two expressions can be carried a little further, and in Table III. the values of

pr_0 or n are shown for the series of salts which give calculated values of K_0 in agreement with Slater's observed values. These have been plotted against the corresponding values of r_0 in fig. 2. The results show that for each group of salts there must be a systematic variation in the exact value to be assigned to n or pr_0 in order to compute the compressibility correctly. It is clear from the arrangement of the plotted points, and also from column 13 of Table I., that the suggested exponential law of repulsion does not

Fig. 2.



quite agree with the experimental data on assuming p to be constant for the series of salts, the dotted line showing the values of pr_0 for $p=3.0 \times 10^8$. The exponential law, however, appears to approximate considerably closer to the observed results than the inverse power law with a single exponent, which would be represented on the diagram by a horizontal line. It is obvious from fig. 2 that the exponent in equation (15) should decrease in some manner as r_0 decreases, a condition that is partially satisfied with the corresponding term pr_0 of equation (14).

The diagram is hardly complete enough to throw much light on the peculiar variations in p , but it appears as though

p might depend to a small extent on the number of electrons involved in the structure of the atom. Thus the group of points for Li or K show that p progressively diminishes with the addition of each ring of electrons in the halogen atoms, and it might be surmized from this that the inner rings have some secondary effect on the force of repulsion.

(7) The results of this paper should be considered somewhat further in relation to the conceptions of Born and his co-workers. Born predicts the compressibilities of certain salts by assuming a form of function for the repulsion for which he chooses, very naturally, the simple inverse function $R = br^{-n}$, where r is the distance between the atom centres. The subsequent calculations lead Born to conclude that the exponent has a value of about 10.

The present writer, on the other hand, is led to regard the repulsion between atoms not as a central force at all, but rather as a quasi-elastic effect analogous to the type of force exerted mutually by two elastic spheres when deformed by being forced together. The repulsion on this view is not a function of r , but is determined by the closeness of approach of the atom "boundaries."

Born has achieved quite successful results in computing certain physical properties theoretically, using his assumed function, and it is not suggested that this function does not mathematically represent the repulsion over a range which is sufficient for his purpose. We have already seen that we can only produce quite a small change in the repulsion by pressure, and it may therefore be suggested that the relation Born assumes does no more than coincide with the true function (whatever this may be) over a certain range of the repulsion in the neighbourhood of the intrinsic repulsion under zero pressure, and that its form is not necessarily in agreement with the physical cause of the repulsion.

The latter criticism of course applies equally to an exponential law, or to any empirical law which happens to agree with the compressibility observations. The justification for suggesting an alternative to Born's inverse power law is, firstly, that the exponential law not only meets the case of any one salt equally well, but also applies better to the series of salts as a whole, and, secondly, that this law is not assumed, but is directly indicated by the experimental data available. Furthermore, in Part II. of the paper it will be seen that an extrapolation of this law, greatly exceeding the range concerned in elasticity observations, can be made successfully in the course of computing certain thermal constants.

Slater⁽⁵⁾ has published some criticisms of Born's law of repulsion, showing that the same exponent n cannot give correct values for the compressibility and for the pressure coefficient at the same time. The writer's criticism is more concerned with the possibility that the independent variable of the inverse function is artificial, much in the way that one could express the velocity of a falling body in terms of its distance from the centre of the earth.

Having assumed the repulsion to be a function of the centre distance of the two atoms, the only way to account for the very great rate of change of the force is by assigning to the exponent a large magnitude, which, as fig. 2 shows, is not in general an integer. As there is a noticeable tendency in recent writings to regard atomic repulsion as an inverse function of the atomic centre distance, it seems desirable to be quite clear as regards the physical limitations of such an assumption. While this conception may often be of service, it should not be allowed to imply any real correspondence with the actual phenomena giving rise to the repulsion.

(8) It is clearly desirable to examine in a similar way the repulsion forces between the atoms of the elements if possible; but the difficulty arises that the nature of the attraction bond is too little understood to allow the direct method used with the alkali halides. It seems certain that the ordinary elastic properties of metals are dependent on the interplay of attractions and repulsions of large numbers of atoms arranged on a space lattice. With this assumption an expression can be derived for the repulsion, containing the constants concerned in the attraction.

If the attraction between two atoms can be expressed as an inverse function of the atomic centre distance such as $\frac{c}{r^n}$, in which c and n are unknown constants, the attraction of the whole lattice on any one atom is the summation of such terms. Since all the attracting atoms lie on the points of a space lattice, we can express this attraction as

$$A = m \frac{c}{r^n} = \frac{a}{r^n}, \quad \dots \quad (16)$$

where m is a summation constant depending on the geometrical type of the lattice.

Equation (2) for the compressibility has been found by Bridgman to apply to most of the metals, and a modification of (3) renders this equation applicable to the cubic lattices

and to the close-packed hexagonal lattice with ideal ratio. The equation becomes

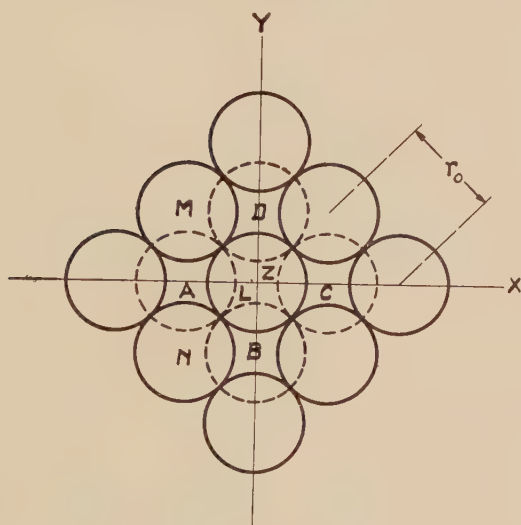
$$F = \gamma P(r_0 - z)^2, \quad . \quad . \quad . \quad . \quad (17)$$

where γ is a constant depending on the lattice and has values as below :

$$\frac{1}{2\sqrt{2}} \text{ face-centred cubic lattice.}$$

$$\frac{1}{\sqrt{3}} \text{ body-centred " "}$$

Fig. 3.



1 simple cubic (NaCl) lattice.

$$\frac{1}{2\sqrt{2}} \text{ close-packed hexagonal lattice.}$$

$$\frac{4}{\sqrt{3}} \text{ tetrahedral (diamond) "}$$

The derivation of the value of γ in one case, the face-centred cubic lattice, may be seen by reference to fig. 3, showing the manner of packing of the atoms, where the full lines represent a layer of atoms in the plane of a cube face, and the dotted lines show an adjacent layer above or below the first.

The packing in any plane consists of a square formation with rows at right angles, and each atom of the next layer is seated in the cavity formed at the centre of the square.

If r_0 denotes the closest approach of the atoms, reduced under a pressure P to $(r_0 - z)$, the number of atoms in unit area of a layer is $\frac{1}{(r_0 - z)^2}$, and the force on an atom such as L in the direction OZ is

$$F_1 = P_z(r_0 - z)^2.$$

The atom L exerts a normal force F on each of its four neighbours A, B, C , and D , components of which are in equilibrium with the external force F_1 , such that

$$F_1 = 4 \frac{F}{\sqrt{2}}.$$

The other component of the force F between the pair such as L and A contributes in a similar way to the equilibrium of L under the pressure P_x , and the same applies to the normal force exerted mutually by every pair of neighbours in the lattice. Hence there is a relation between the external pressure and the increment of the repulsion between adjacent atoms, given by

$$F = \frac{1}{2\sqrt{2}} P(r_0 - z)^2. \quad (18)$$

Proceeding just as in section 3 from this point, we can derive an expression for the repulsion having the form

$$R = \frac{a}{r_0^n} + \left(\frac{na}{r_0^{n+1}} + \frac{3\gamma r}{K_0} \right) z + \left(\frac{n(n+1)a}{2r_0^{n+2}} + \frac{9\gamma\lambda}{2K_0^2} z - \frac{9\gamma}{2K_0} \right) z^2. \quad (19)$$

This is a more general form of equation (10), to which it reduces as a particular case on putting $n=2$, $a=\beta e^2$, and $\gamma=1$.

Of the two unknown attraction constants a and n , a is the most troublesome, and a possible method of eliminating it is employed below. The exponent n is only unknown in the limited sense that its exact value is uncertain. There is a growing body of indirect evidence that it must be greater than 2, some writers asserting that it must exceed 3, and that of numbers exceeding this 4 is the most probable. An exponent 4 accords with the induced or permanent dipole theory of atomic attraction, and it is also the value indicated

by the well-known dimensional argument⁽⁸⁾ based on the cohesion pressure term $\frac{a}{v^2}$ in van der Waals's equation of state. Further, it is the value in best general agreement with deductions from surface tension phenomena. In the following treatment a value 4 will therefore be assigned provisionally to the exponent, thus following the course adopted by Sutherland⁽⁹⁾ and by Grüneisen⁽¹⁰⁾ in their respective theories of the solid state.

The other constant a may be eliminated in the following way :—On account of the universal attraction of the atoms for one another, the atoms in the lattice are forced tightly together as if under a uniform pressure. This has been called the intrinsic pressure, and it corresponds to the ideal or intrinsic tenacity of the material. Denoting the intrinsic pressure by π_0 , we have the previous relation between A and π_0 ,

$$A = \frac{a}{\gamma^n} = \gamma \pi_0 r_0^3. \quad . \quad . \quad . \quad . \quad (20)$$

As it is possible to compute π_0 from known physical constants of the metals, $\frac{a}{r_0^n}$ can be eliminated from each of the coefficients of equation (19), leaving it in the form

$$\begin{aligned} R = \gamma \left[\pi_0 r_0^2 + \left(n \pi_0 r_0 + \frac{3r_0}{K_0} \right) z + \left(\frac{n(n+1)\pi_0}{2} + \frac{9\lambda}{2K_0^2} - \frac{9}{2K_0} \right) z^2 \right] \\ = L + Mz + Nz^2. \quad . \quad . \quad . \quad (21) \end{aligned}$$

In this form the constant a has disappeared, and, moreover, n no longer appears as an exponent but only as a factor, in which form the uncertainty as to its true value has considerably less effect, as will be apparent later from the numerical values calculated for the separate terms above.

(9) To obtain an estimate of the value of π_0 consider unit volume of the material receiving a small increment of heat with a rise of temperature δT . If δE is the increment of internal kinetic energy, and δV the increment of volume, we have

$$J s \rho . \delta T = \delta E + \pi_0 \delta V + P . \delta V,$$

in which s and ρ are the specific heat and specific gravity and P is the external pressure. It is assumed in this equation that ordinary temperatures are concerned at which the kinetic energy of free electrons may be neglected, and at

the same time the temperature is not low enough to introduce quantum considerations. If the equipartition principle is applied to the potential and kinetic energies of the atoms $\pi_0 \delta V$ is the increment of potential energy, and it will be equal to δE . At atmospheric pressure P is negligible compared with π_0 , and therefore

$$\pi_0 \delta V = \frac{1}{2} J s \rho \cdot \delta T$$

and

$$\frac{\delta V}{\delta T} = 3\alpha,$$

or

$$\pi_0 = \frac{J s \rho}{6\alpha}, \quad . \quad . \quad . \quad . \quad . \quad (22)$$

if α is the linear coefficient of expansion.

Other estimates of the intrinsic pressure have been made at different times, and a comparison of the results yielded by equation (22) with these will be made. In Table IV. the values of the intrinsic pressure for a number of materials are given as obtained by different methods, the second column showing π_0 calculated from equation (22). In the further columns the values found by other writers are given, together with the ratio of each pressure to π_0 .

Traube⁽¹¹⁾ determined the intrinsic pressure by assuming van der Waals's equation of state to be applicable to solids.

The cohesion pressure is then found from the term $\frac{a}{v^2}$, which was computed by Traube, with the results shown in column 3. The series of ratios are fairly closely constant, showing that the relative values of π_0 agree with Traube's results, but the magnitude of the intrinsic pressure π_0 is rather greater.

Richards⁽¹²⁾ obtains the intrinsic pressure from an expression $\frac{R}{3V\alpha}$, in which R is the gas constant, V is the atomic volume, and α is again the linear coefficient of expansion. This expression is derived from an empirical equation of the solid state suggested by Richards, and it is interesting to notice that it may be readily transformed into a form closely resembling equation (22). If the atomic heat is taken as $3R$, the expression becomes $\frac{sA}{9V\alpha}$ or $\frac{J s \rho}{9\alpha}$ if thermal units are used for s as before. This is identical with (22) except as regards the numerical factor, which is only $2/3$ that found in (22). It is therefore not surprising to find the column of ratios

TABLE IV.

Material.	$\pi_0 = \frac{J \rho}{C a}$.		Traube.		Richards.		Grüneisen.		Harkins and Hall.	
	1.	2.	$\frac{a}{v^2}$.	Ratio to π_0 .	$\frac{R}{3V a}$.	Ratio to π_0 .	—	Ratio to π_0 .	$\frac{T_m}{V}$.	Ratio to π_0 .
			3.	4.	5.	6.	7.	8.	9.	10.
Aluminium		1.79×10^{11}	1.18×10^{11}	0.66	1.26×10^{11}	0.705	—	—	89.5	50×10^{-11}
Cobalt		5.29	—	—	3.29	0.625	—	—	262	49.5
Nickel		5.22	2.80	0.535	3.27	0.625	—	—	258	49.5
Copper		3.50	2.33	0.665	2.42	0.69	6.02×10^{11}	1.15	191.3	54.7
Palladium		4.06	2.24	0.55	2.79	0.685	5.37	1.53	207	51
Silver		2.18	1.26	0.58	1.45	0.665	—	—	120	55
Iridium		7.91	—	—	5.03	0.635	2.83	1.32	300	38
Platinum		5.45	3.20	0.585	3.47	0.635	—	—	223	41
Gold		2.98	1.76	0.59	1.89	0.635	5.62	1.03	129.4	43.5
Lead		0.86	0.51	0.595	0.53	0.615	—	—	33	38.4
Tungsten		10.0	—	—	6.32	0.63	0.89	1.03	351	35.1
Molybdenum ..		10.0	—	—	5.90	0.59	9.95	0.99	268	26.8
Iron		5.0	3.20	0.64	3.45	0.69	6.27	0.63	254	50.8
Zinc		1.56	—	—	1.02	0.655	6.25	1.25	75.2	48
Cadmium		1.12	0.722	0.645	0.72	0.61	1.46	0.93	45.6	40.5
Tantalum		6.80	—	—	4.24	0.625	0.82	0.73	257	38
Tin		1.31	0.678	0.52	0.81	0.62	—	—	31	23.5
							2.06	1.57		

so constant in this case, the variation to be observed being due to departures from the law of Dulong and Petit, and to some extent to differences in the values assigned to α in the two cases.

Grüneisen⁽¹⁰⁾ has developed a theory of the solid state which is probably the most successful attempt made up to the present to correlate physical properties of the monatomic elements with atomic forces. Grüneisen's theory can be applied to give values of the intrinsic pressure as shown in column 7. Most of these values have been obtained from a lecture on the subject of cohesion by Dushman⁽¹³⁾, the values for tin and lead only having been added by the writer. The calculation of the intrinsic pressure by this theory involves a knowledge of the latent heat of vaporization, which is a drawback, owing to the meagre data available. It will be seen that equation (22) gives values of the pressure which on the average agree fairly closely with these.

Another method of estimating the relative values of the intrinsic pressure is due to Harkins and Hall⁽¹⁴⁾, who consider that $\frac{T_m}{V}$ is a measure of the pressure, T_m being the absolute melting-point. This formula is derived from the well-known melting-point equation suggested by Lindemann. The necessary constant to enable this formula to yield actual values of the intrinsic pressure was not given by Harkins and Hall, and only a series of proportional values are therefore given in the table, but these are, on the whole, in good agreement with the π_0 values as shown by the ratios. It is interesting to notice that the above formula, as in the case of Richard's expression, can be shown to be approximately the same as equation (22). It is known to be an empirical rule, sometimes called Pictet's rule, that the product of the absolute melting temperature and the coefficient of expansion of most of the elements is constant with a fair degree of approximation. The product of the atomic weight and the specific heat is also closely constant (Dulong and Petit's law). Hence equation (22) may be modified as follows, if m is the atomic weight:—

$$\begin{aligned}\pi_0 &= \frac{J s \rho}{6 \alpha} = \frac{J(s m) T_m}{6 \frac{m}{\rho} (\alpha T_m)} = \frac{J(s m)}{6 (\alpha T_m)} \times \frac{T_m}{V} \\ &= \text{const} \times \frac{T_m}{V}.\end{aligned}$$

TABLE VI.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
Material.	r_0 .	K_0 .	λ .	π_0 .	$\pi_0 \gamma r_0^2$.	$n \pi_0 \gamma r_0$.	$\frac{3r_0 \gamma}{K_0}$.	$\frac{n(n+1)\pi_0 \gamma}{2}$.	$\frac{9\lambda \gamma}{2K_0^2}$.	$\frac{9\gamma}{2K_0}$.	L.	M.	N.	$p = \frac{M}{L}$.	$p = \sqrt{\frac{2N}{L}}$.
A. Aluminium	2.86×10^{-8}	1.334×10^{-12}	5.35×10^{-12}	1.79×10^{11}	0.517×10^{-4}	0.725×10^4	2.27×10^4	0.63×10^{12}	4.79×10^{12}	1.19×10^{12}	0.517×10^{-4}	2.995×10^4	4.23×10^{12}	5.8×10^8	4.04×10^8
Cobalt	2.51	0.54	7.9	5.29	1.18	1.88	4.93	1.87	43.0	2.94	1.18	6.81	41.93	5.77	8.42
Nickel	2.50	0.529	8.1	5.22	1.155	1.85	5.00	1.845	46.0	3.01	1.155	6.85	44.83	5.94	8.80
Copper	2.54	0.72	7.5	3.50	0.797	1.256	3.74	1.235	23.0	2.21	0.797	5.00	22.02	6.27	7.43
Palladium	2.73	0.53	8.1	4.06	1.07	1.565	5.47	1.43	45.8	3.00	1.07	7.03	44.23	6.55	9.08
Silver	2.88	0.99	9.2	2.18	0.64	0.89	3.08	0.735	14.9	1.605	0.64	3.97	14.02	6.20	6.62
Iridium	2.70	0.263	10.1	7.91	2.04	3.02	10.70	2.79	224.0	5.95	2.04	13.72	220.8	6.73	14.7
Platinum	2.77	0.36	10.2	5.45	1.48	2.13	8.15	1.925	125.0	4.42	1.48	10.28	122.5	6.95	12.84
Gold	2.88	0.577	7.3	2.98	0.875	1.213	5.30	1.05	34.8	2.75	0.875	6.51	33.1	7.34	8.68
Lead	3.43	2.30	11.0	0.86	0.367	0.422	1.60	0.302	3.3	0.69	0.367	2.02	2.91	5.50	3.98
Calcium	3.97	5.70	18.4	0.65	0.362	0.365	0.74	0.23	0.9	0.28	0.362	1.10	0.85	3.04	2.17
Rhodium	2.70	0.372	14.3	6.15	1.58	2.35	7.7	2.17	164	4.3	1.585	10.05	161.9	6.36	14.3
Thorium	3.56	1.82	14.0	2.0	0.90	1.01	2.08	0.71	6.71	0.87	0.90	3.09	6.55	3.44	3.81
B. Iron	2.49	0.537	7.0	5.0	1.79	2.87	7.43	2.88	53.8	4.47	1.79	10.30	52.2	5.79	7.63
Tungsten	2.73	0.315	10.2	10.05	4.31	6.33	15.0	5.79	267.0	8.25	4.31	21.33	263.6	4.95	11.08
Tantalum	2.83	0.479	1.0	6.8	3.14	4.45	10.2	3.92	11.3	5.43	3.14	14.65	9.8	4.67	2.50
Molybdenum	2.72	0.361	5.8	6.0	2.54	3.75	13.0	3.44	115.5	7.2	2.54	16.75	111.7	6.59	9.38
Lithium	3.03	9.0	22.4	0.588	0.312	0.411	0.585	0.339	0.720	0.289	0.312	0.996	0.77	3.19	2.22
Sodium	3.72	15.8	78	0.307	0.245	0.263	0.408	0.177	0.815	0.165	0.245	0.671	0.827	2.74	2.60
Potassium	4.50	32.1	230	0.148	0.173	0.154	0.243	0.085	0.582	0.081	0.173	0.397	0.586	2.30	2.60
Rubidium	4.93	40.5	172	0.095	0.133	0.108	0.211	0.055	0.273	0.064	0.133	0.319	0.264	2.40	1.99
Cæsium	5.35	62.0	260	0.073	0.120	0.090	0.150	0.042	0.176	0.042	0.120	0.240	0.176	2.00	1.71
Chromium	2.51	0.52	8.4	6.5	2.36	3.77	8.36	3.75	80.5	5.0	2.36	12.13	78.7	5.15	8.15
Vanadium	2.63	0.61	8.4	4.46	1.78	2.71	7.48	2.58	58.6	4.25	1.78	10.19	56.9	5.72	8.00
C. Cadmium	2.96	1.95	11.0	1.12	0.347	0.47	1.61	0.396	4.60	0.818	0.347	2.08	4.178	6.00	4.91
Magnesium	3.22	2.96	13.6	1.17	0.430	0.535	1.15	0.414	2.48	0.537	0.430	1.685	2.357	3.92	3.31
Cerium	3.65	3.57	10.6	0.93	0.438	0.48	1.09	0.325	1.33	0.445	0.438	1.57	1.21	3.58	2.35
Zinc	2.67	1.50	—	1.55	0.390	0.587	1.89	—	—	—	0.390	2.477	—	6.35	—
Beryllium	2.25	0.855	9.03	7.6	1.36	2.42	2.79	2.63	19.8	1.86	1.36	5.21	20.6	3.84	5.5
Titanium	2.95	0.80	—	3.2	0.99	1.34	3.92	—	—	—	0.99	5.26	—	5.32	—
Zirconium	3.20	1.10	13.5	2.47	0.89	1.12	3.08	0.87	17.7	1.45	0.89	4.20	17.1	4.72	6.20
G. Germanium	2.44	1.33	9.8	1.95	2.68	4.39	12.22	4.50	53.4	7.53	2.68	16.6	50.3	6.2	6.29
Diamond	1.54	0.16	—	23.2	12.7	33.0	66.5	—	—	—	12.7	99.5	—	7.85	—
Indium	3.24	2.7	—	1.15	1.21 γ	1.49 γ	3.6 γ	—	—	—	1.21 γ	5.09 γ	—	4.21	—
Manganese	2.67	0.79	13.4	4.33	3.09 γ	4.62 γ	10.1 γ	4.33 γ	96.8 γ	5.7 γ	3.09 γ	14.72 γ	95.4 γ	4.77	7.85

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1.	2.	3.	4.	5.
Material.	n_0 .	K_0 .	λ .	π_0 .
A. Aluminium	2.86×10^{-8}	1.334×10^{-12}	5.35×10^{-12}	1.79×10^{11}
Cobalt	2.51	0.54	7.9	5.29
Nickel	2.50	0.529	8.1	5.22
Copper	2.54	0.72	7.5	3.50
Palladium	2.73	0.53	8.1	4.06
Silver	2.88	0.99	9.2	2.18
Iridium	2.70	0.268	10.1	7.91
Platinum	2.77	0.36	10.2	5.45
Gold	2.88	0.577	7.3	2.98
Lead	3.48	2.30	11.0	0.86
Calcium	3.97	5.70	18.4	0.65
Rhodium	2.70	0.372	14.3	6.15
Thorium	3.56	1.82	14.0	2.0
B. Iron	2.49	0.587	7.0	5.0
Tungsten	2.73	0.315	10.2	10.05
Tantalum	2.83	0.479	1.0	6.8
Molybdenum.....	2.72	0.361	5.8	6.0
Lithium	3.03	9.0	22.4	0.588
Sodium	3.72	15.8	78	0.307
Potassium	4.50	32.1	230	0.148
Rubidium	4.93	40.5	172	0.095
Cæsium	5.35	62.0	260	0.073
Chromium.....	2.51	0.52	8.4	6.5
Vanadium	2.63	0.61	8.4	4.46
C. Cadmium	2.96	1.95	11.0	1.12
Magnesium	3.22	2.96	13.6	1.17
Cerium	3.65	3.57	10.6	0.93
Zinc	2.67	1.50	—	1.55
Beryllium	2.25	0.855	9.08	7.6
Titanium	2.95	0.80	—	3.2
Zirconium	3.20	1.10	13.5	2.47
G. Germanium	2.44	1.38	9.8	1.95
Diamond	1.54	0.16	—	23.2
Indium	3.24	2.7	—	1.15
Manganese	2.67	0.79	13.4	4.33

The mean value of αT_m is about 0.02, and sm is closely equal to 6.0; hence the constant has a numerical value approximately $2 \cdot 10 \times 10^9$.

The method of computing π_0 resulting in equation (22) has the advantage of being very simple and direct, and requires a knowledge of only very well-determined physical constants. Table IV. proves that it yields a series of results for the relative magnitudes of the intrinsic pressure in quite good agreement with three other series of estimates, and it also gives absolute magnitudes of pressure not greatly different from those of Traube and Richards, and still more nearly equal to those derived from Grüneisen's theory. As it is of considerable importance to the later deductions of this paper that the most reliable values possible should be used for the intrinsic pressure, a further test will be imposed on the validity of equation (22). The intrinsic pressures of the alkali halide series of salts can be found quite readily

from the intrinsic attraction L or $\frac{\beta e^2}{r_0^2}$ on each atom in the lattice. Equation (20) then gives the intrinsic pressure to be $\pi_0 = \frac{L}{r_0^2}$, and by using the values of L from Table I.

these may be compared with the results obtained from equation (22), as shown in Table V.

A comparison of the two values of the intrinsic pressure in this table shows on the whole quite a good agreement, having regard to the complete difference between the two methods of deriving the pressure. These results therefore provide a useful confirmation of the general validity of the formula in equation (22).

(10) The various terms in the coefficients of equation (21) can now be computed for a number of metals for which compressibility data are available, assigning a provisional value 4 to the exponent n . These are tabulated in the various sections of Table VI., together with the values of r_0 , K_0 , and λ . The latter are principally the well-known determinations of Bridgman. The table has been arranged in four groups of metals having (A) the face-centred cubic lattice, (B) the body-centred cubic lattice, (C) the hexagonal lattice, (D) other lattices.

An examination of the numerical values of the coefficients L , M , and N indicates, taking the table as a whole, that these are fairly closely related to one another, in the same

TABLE V.

	F.		Cl.		Br.		I.	
	$\pi_0 = \frac{L}{r_0^2}.$	$\pi_0 = \frac{Jsp}{6a}.$	$\pi_0 = \frac{L}{r_0^2}.$	$\pi_0 = \frac{Jsp}{6a}.$	$\pi_0 = \frac{L}{r_0^2}.$	$\pi_0 = \frac{Jsp}{6a}.$	$\pi_0 = \frac{L}{r_0^2}.$	$\pi_0 = \frac{Jsp}{6}.$
Li	3.59×10^{11}	2.22×10^{11}	1.51×10^{11}	1.00×10^{11}	0.85×10^{11}	0.67×10^{11}	0.605×10^{11}	0.47×10^{11}
Na	2.30	1.57	1.05	0.845	0.565	0.545	0.425	0.39
K	1.31	1.04	0.685	0.67	0.485	0.52	0.37	0.36
Rb	—	—	0.58	0.595				

manner as the corresponding coefficients in the following expansion of an exponential expression for the repulsion,

$$R = Le^{pz} = L + pLz + \frac{p^2}{2!} Lz^2 + \dots \quad (23)$$

By equating the coefficients, we have

$$pL = M \quad \text{or} \quad p = \frac{M}{L},$$

$$\frac{1}{2}p^2L = N \quad \text{or} \quad p = \sqrt{\frac{2N}{L}}.$$

In the last two columns these two values of p are given, and in general there is a fairly good agreement in order of magnitude. For some metals, notably the less compressible

metals, p as computed from $\frac{2N}{L}$ exceeds the value $\frac{M}{L}$, and

in other cases it is less. It is not to be expected that a very precise numerical agreement could be obtained, as the predominating term in N involves the coefficient of variation of compressibility with pressure, the exact determination of which must present great difficulty, especially with the harder metals. The general correlation of the coefficients throughout the table, however, appears to be such as to suggest that the empirical exponential law of repulsion, previously deduced in a similar way for the alkali halides, may apply also to the atoms of the metals.

In a few cases in the table there are not enough data available to enable N to be computed, but it was thought worth while to include these metals for the sake of the values of the constants L and p , assuming that the same type of law is applicable. In certain cases the value of r_0 is somewhat uncertain. Rubidium and caesium, for example, have been included in group B because their compressibility constants are well determined, although their atomic distances have not so far been measured directly. The values assigned to r_0 are therefore those corresponding to their densities, assuming them to have the same lattice structure as the rest of the alkali metals. Most of the metals in group C approximate closely to the ideal close-packed arrangement, but zinc and cadmium are exceptional and have axial ratios differing considerably from the ideal value, and some uncertainly must be acknowledged in the calculated coefficients for these two metals. In this group the coefficient N for titanium has not

been included, because the pressure coefficient λ has been found by Bridgman to be quite anomalous.

In group D indium and manganese have been included, although there is again some uncertainty as to the value of r_0 . These metals crystallize in a slightly deformed type of face-centred cubic lattice, having two values of the closest approach not quite the same. For the same reason the value of γ is uncertain, but since γ occurs as a factor of every term in equation (21) it is still possible to calculate the ratios of the coefficients shown in the last two columns, and so derive values of p . For these two metals the various terms are tabulated as the product of γ into a numerical factor.

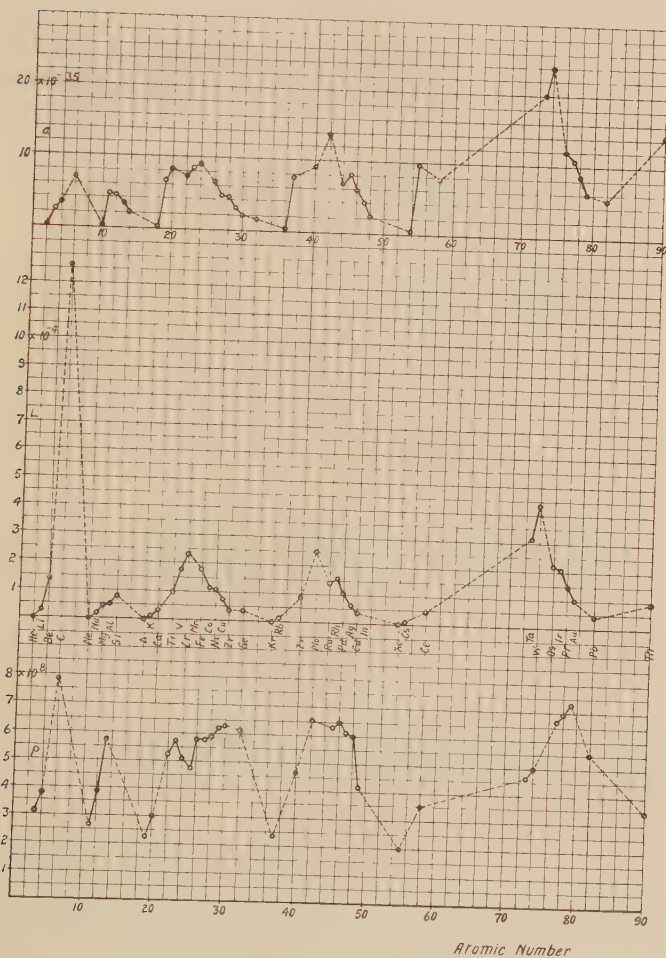
The effect of a possible error in assuming the attraction exponent to be 4 can now be judged from the numerical values given in Table VI. In the term for L, n does not appear, and in M it appears as a factor in only one of the terms $n \pi_0 \gamma r_0$, which in magnitude is always smaller (from $\frac{1}{2}$ to $\frac{1}{4}$) than the other term $\frac{3r_0\gamma}{K_0}$. In the coefficient N the

exponent plays a still less important part. A certain latitude is therefore possible in the value of n without seriously disturbing the relation between the coefficients, and the reasoning which leads to the suggestion of an exponential law does not entirely stand or fall according to the exact validity of the assumption $n=4$.

The variations in the values of the two constants L and p amongst the elements are of considerable interest. The intrinsic attraction L being equal to $\frac{a}{r^n}$ is clearly to a large extent determined by the size of the atom, and depends also on the fundamental attraction constant a . The values of L, p , and a have been plotted against the atomic number of the elements in fig. 4, and each constant shows a well-defined periodicity. The variations in L are the greatest, and considerably exceed those in a , because, as is well known, there is a certain amount of periodic variation in the size of the atoms, which is enhanced when r is raised to the fourth power. A periodic variation in the two fundamental constants p and a is to be expected, because it is well known, and has been discussed in detail by Harkins and Hall⁽¹⁴⁾, that all the principal cohesive properties of solids vary periodically with the atomic number. Such properties as elasticity, tenacity, atomic volume, thermal expansion, melting-point, etc., must be intimately related to the magni-

tude and character of the forces between atoms, and it would be difficult to accept a series of atomic force constants that was not periodic with atomic number.

Fig. 4.



In plotting the curves of fig. 4 some elements have been included which do not appear in Table VI.; these are elements for which L and a can be calculated, but not p . In a few cases L has been determined from the formula for π_0 given by Harkins and Hall with the constant $2 \cdot 10 \times 10^9$

derived in this paper. These are comparatively rare elements, such as cerium and germanium, for which the physical constants employed in equation (22) are not all known, but for which the melting-point is known. In the curves for L and α the noble gases have also been included by assigning to them conjectural values much smaller than the smallest of the other elements plotted. These elements are known to exert very little atomic attraction by comparison with the elements, and their relative positions on the curve, all placed nearly at zero, cannot be far wrong for the purpose of the graphs. It is desirable to include these elements on account of their important function in defining the groups of the periodic system.

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- (3) Phil. Mag. xxxii. pp. 31, 215, 524 (1891).
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PART II.

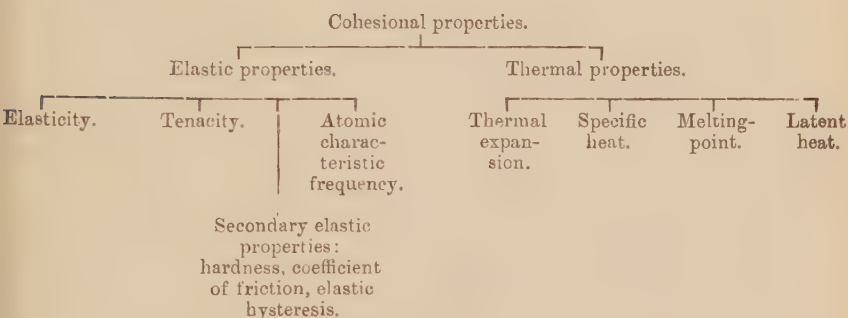
(1) In Part I. of this paper it has been shown that the repulsion between neighbour atoms in a space lattice can be expressed empirically as an exponential function,

$$R = Le^{pz},$$

in which the variable z is the relative displacement of the atoms under an external force. The constant L is the intrinsic repulsion when under no stress. This equation was derived from elasticity data, assuming that the attraction on an atom can be expressed as an inverse function $A = ar^{-n}$, the exponent being taken as 2 in the case of the ionic lattice of the NaCl type, and 4 in the case of the metal lattices.

Part II. of the paper starts by accepting these two laws of force as being at least approximately correct, with the values previously calculated for the constants, and attempts to apply

the laws to the derivation of certain physical properties of solids by first principles. It may therefore be regarded either as a tentative attempt to develop a theory of the solid state based upon the fundamental forces exerted between atoms, or, alternatively, as a further and rather searching test of the validity of the above supposed laws of force. There can be little doubt that all the cohesive properties of solids depend primarily on the characteristics of the basic atomic forces. The properties concerned are shown in a tabular diagram below :—



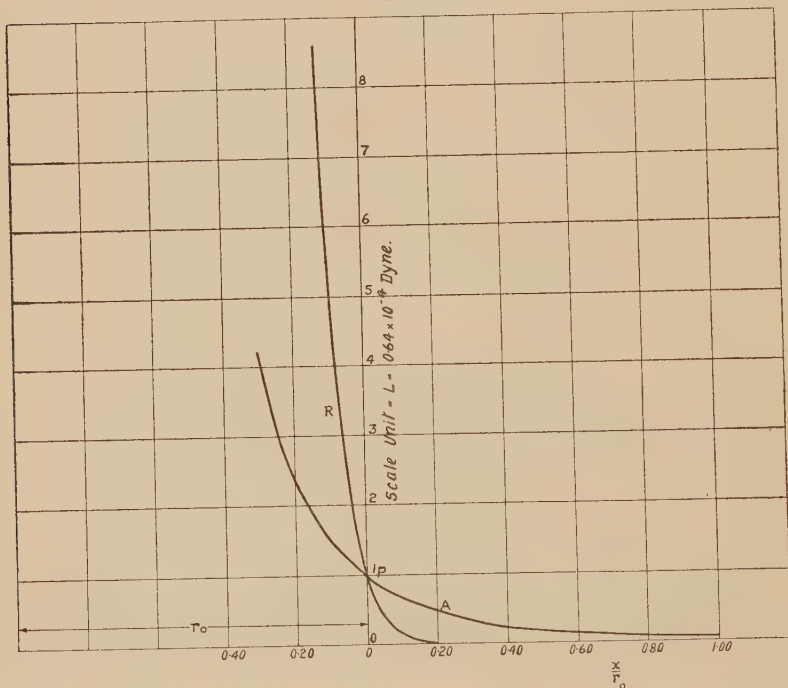
The cohesive properties fall into two groups of elastic and thermal properties, and each property has a physical constant associated with it, such as the modulus of elasticity, the coefficient of expansion, etc. As many as possible of these physical constants will be computed from the assumed attraction and repulsion laws. Also certain relationships known to exist amongst the physical properties, such as Pictet's rule that the product of the coefficient of expansion and the melting temperature is constant, will be derived directly from the atomic forces.

(2) Elasticity.

The elastic relation between stress and strain is a consequence of the resistance offered by two adjacent atoms to a relative displacement. If two atoms are displaced by a small amount δx , a force is required acting along the line of centres of amount $\left(\frac{dR}{dx} - \frac{dA}{dx}\right)\delta x$. The actual repulsion and attraction curves for a typical metal (silver) are shown in fig. 5, which may help in considering the rates of change of the forces. These curves are shown true to scale, and were

computed from the laws assumed for each force, with the constants previously derived in Part I. The independent variable is the proportional relative displacement x/r of the two atoms from the condition of zero stress. Under all ordinary conditions $\frac{dR}{dx}$ considerably exceeds $\frac{dA}{dx}$, and the above force is therefore always a restoring force. Stress is the effective summation of such atomic forces.

Fig. 5.



For simplicity we shall calculate the modulus of compressibility, as in this case the elastic strain involves no lattice distortion and all pairs of atoms receive the same treatment. We have already seen in equation (17) of Part I. that the normal force between two adjacent atoms in a lattice, arising from an external pressure P , is $Pr_0^2\gamma$, and therefore

$$Pr_0^2\gamma = \left(\frac{dR}{dx} - \frac{dA}{dx} \right) \delta x.$$

The linear strain is $\frac{\delta x}{r_0}$, and the volumetric strain is therefore $\frac{3\delta x}{r_0}$, from which the modulus of compressibility is

$$C = P / \frac{3\delta x}{r_0} = \frac{1}{3r_0\gamma} \left(\frac{dR}{dx} - \frac{dA}{dx} \right). \quad (1)$$

Using the assumed expression for R and A

$$R = L\epsilon^{px},$$

$$\frac{dR}{dx} = pL\epsilon^{px},$$

and

$$A = \frac{a}{r^n},$$

$$\frac{dA}{dx} = \frac{dA}{dr} = \frac{na}{r^{n+1}}.$$

When the displacement of the atoms is small these become

$$\frac{dR}{dx} = pL \quad \text{and} \quad \frac{dA}{dx} = \frac{nA}{r_0} = \frac{nL}{r_0},$$

from which

$$C = \frac{L}{3r_0^2\gamma} (pr_0 - n), \quad (2)$$

an expression for the modulus entirely in terms of atomic constants. It may be observed that for the metals pr_0 has a value ranging from about 15 to 21, hence any uncertainty in assuming a value 4 for the exponent n has only a comparatively small effect on the result.

As regards the calculated values of the modulus, these will necessarily be in agreement with the values found experimentally, since the calculation is the converse of that by which the exponential law of repulsion was derived. Our present object, however, is to ascertain in how many respects the assumed laws of attraction and repulsion lead to agreement with observed physical constants. Of these the elastic constants are an important group, and must therefore be included. The fact that an agreement in this case is expected does not affect its evidential value as a particular result derived from the hypotheses.

The property of elasticity is mainly conferred by the characteristics of the repulsion, and reasons have been given earlier for considering the repulsion to be a quasi-elastic

non-central force resisting very strongly any attempt to deform the atom. The gradient $\frac{dR}{dx}$ of this force may therefore be regarded as a fundamental elastic constant of the atom, and it is the chief contributor in equation (1) to the elastic modulus, the part played by $\frac{dA}{dx}$ being smaller and more incidental.

It is interesting to notice in what way the theory indicates that Hooke's law should hold, although the repulsion curve in fig. 5 is by no means linear. The actual atomic displacement δx for any ordinary stress can be computed from equation (1), and, as an actual example, in silver under a stress of 10,000 lb. per square inch $\frac{\delta x}{r}$ has a value 0.00023.

In fig. 5 this displacement is so small that it is impossible to show it to scale in the figure. In other words, any elastic stress we may apply produces only a very small change in the intrinsic force OP exerted by the atoms, and the elasticity is determined almost entirely by the single value of $\frac{dR}{dx}$ at the point P , with a close proportionality between stress and strain.

(3) Tenacity.

In attempting to derive the tenacity of a solid from assumed atomic forces it is clearly the intrinsic tenacity and not the practical tenacity that must be considered. The practical tenacity falls far short of the ideal value which would follow as a result of the cohesive forces, and a direct comparison of the magnitudes of the calculated values and the values observed experimentally cannot be made.

Defining the ideal tenacity f as the triple tensile stress necessary to tear the atoms asunder by overcoming the intrinsic attraction between them, we can express this stress as

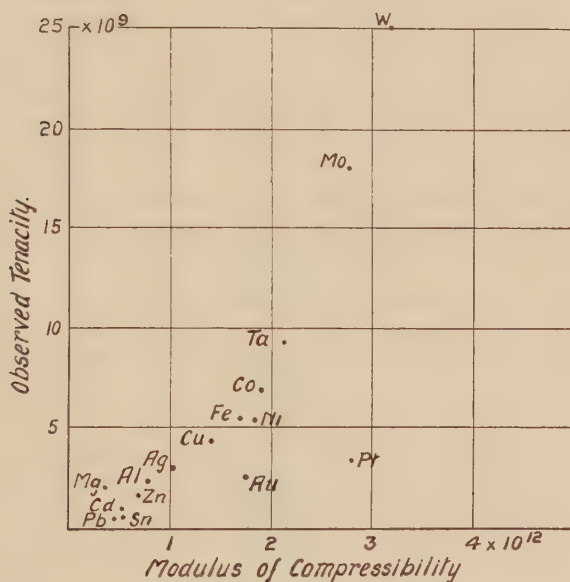
$$f = \frac{L}{\gamma r_0^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

by the same reasoning as before. Referring to equation (2), f can be written in the form

$$f = \frac{3}{pr_0 - n} C. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Since the product pr_0 varies only slightly throughout the metals, this equation implies that according to the theory there should be an approximate proportionality between the tenacity and the elastic modulus of the metals. A broad relationship of this kind is actually found to occur between the observed tenacity and the modulus, as shown by fig. 6. Certain marked exceptions occur, such as gold and platinum, and tenacity in general is so variable according to the treatment of the metal that any exact comparison with the theory is impossible. Qualitatively, however, the theory is in agree-

Fig. 6.



ment with the well-known observed fact that tenacity and hardness tend to increase proportionally with the elastic constants.

(4) Atomic vibration frequency.

The vibration frequency of the atoms characteristic of the different elements is known approximately, various methods being available for its determination. The frequency of linear vibrations will depend entirely on the mass of the atom and on the type of forces exerted by adjacent atoms, and the frequencies calculated from our hypothetical forces of repulsion and attraction can be compared with the

accepted values. In the simple ideal case of two atoms in equilibrium under the mutual attraction and repulsion a small displacement will give rise to oscillations having a frequency

$$n = \frac{1}{2\pi} \sqrt{\frac{\frac{dR}{dx} - \frac{dA}{dx}}{m}},$$

where m is the mass of the atom.

In an actual metal each atom has a number of neighbours all exerting a controlling force upon it, and if we consider the actual case of the face-centred cubic lattice in fig. 3, Part I., and imagine the atom L to be displaced slightly along the Z-axis, eight of its twelve neighbours exert a restoring force. These are the atoms A, B, C, and D, together with four similarly situated atoms in the layer on the opposite side of L. The total restoring force in the direction of the Z-axis is then $8 \cos^2 45^\circ \left(\frac{dR}{dx} - \frac{dA}{dx} \right)$ per unit displacement, and the frequency is therefore

$$n = \frac{1}{2\pi} \sqrt{\frac{4 \left(\frac{dR}{dx} - \frac{dA}{dx} \right)}{m}} \quad \dots \dots (5)$$

$$= \frac{1}{2\pi} \sqrt{\frac{4 \left(pL - \frac{n}{r_0} L \right)}{m}}$$

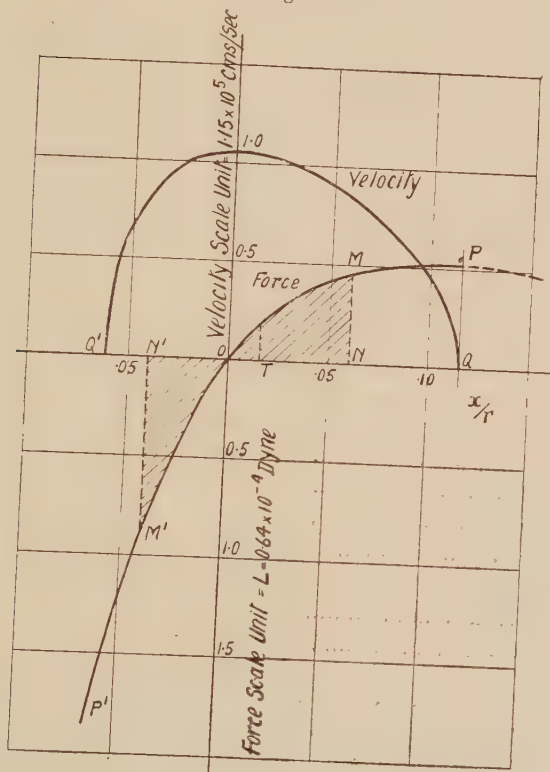
$$= \frac{1}{2\pi} \sqrt{\frac{4L(pr_0 - n)}{mr_0}} \quad \dots \dots (6)$$

The numerical factor $8 \cos^2 45^\circ$ corresponds to a displacement of an atom in any of the three directions perpendicular to the elementary lattice cube face, and it may be noted that the similar factor found for the other eight principal directions, viz., perpendicular to the cube edges and along the cube diagonals, has in each case the same value 4. Equation (6) may therefore be taken as the ideal value of the natural frequency of the atom for small displacements.

Two different causes arise which may to some extent modify the frequency so found. The first is that the twelve adjacent atoms are themselves in vibration and the actual system of forces exerted at any instant on the atom L may differ widely from the ideal system depicted above. As a result the vibration frequencies of the atoms must be spread

out over a considerable band and the frequency of any particular atom almost certainly is constantly changing. There is, however, a statistical value of the most probable frequency, which is the frequency concerned whenever some physical phenomenon is associated with atomic vibrations, and equation (6) may be taken as representing this mean value of all the atoms.

Fig. 7.



The second consideration is that the amplitude of the vibration is not generally so small that the motion can be assumed to be harmonic. The curves of fig. 5 and of fig. 7 show clearly that the restoring force is not at all proportional to the displacement. In the latter figure the curve POP' is the restoring force A—R plotted against displacement for the silver atom, the units being L and r respectively. The vibratory motion will not be symmetrical about the point of

equilibrium O, and if ON is the semiamplitude in one direction, that in the opposite direction will be ON', determined by the fact that the potential energy OM'N' must equal that at the other rest point OMN. For any value of the full amplitude, such as NN', the velocity of the atom at every position can be readily found, and from this the periodic time of the vibration can be calculated. The velocity curve for an amplitude QQ' is shown plotted in fig. 7. This represents the critical amplitude when the restoring force PQ reaches a maximum, or when $\frac{dA}{dx} = \frac{dR}{dx}$ and the stability of

TABLE I.

Metal.	Atomic vibration frequency.	
	Calculated.	Accepted value.
Aluminium	7.17×10^{12}	7.5×10^{12}
Cobalt	7.12	8.2
Nickel	7.23	8.2
Copper	5.97	6.7
Palladium	5.58	5.74
Silver	4.16	4.36
Iridium	5.79	4.9
Platinum	5.04	4.36
Gold	4.00	3.4
Lead	2.16	1.84
Zinc	4.20	4.36
Magnesium	5.38	7.20
Cadmium	2.96	3.0
Cerium	2.18	2.64

the atoms vanishes. In a later section this condition is regarded as determining the melting-point. This curve exhibits clearly the asymmetrical character of the vibration. On computing from the curve the periodic time, it is found to be only 1.17 times as great as that given by equation (6) for small amplitudes, although an extreme case has been taken. Hence under more ordinary conditions of temperature the error involved in accepting this equation is not likely to exceed a small percentage. Equation (6) has therefore been used to calculate a series of characteristic atomic frequencies as given by the assumed laws of repulsion and attraction. These appear in Table VII. together with the commonly accepted values⁽¹⁾.

It appears from these results that the assumed atomic forces lead to vibration frequencies closely of the same order as those deduced by other methods. The relative magnitude of the frequency throughout the group of metals also agrees fairly well with that observed among the accepted values. The differences which occur between the two columns are, in fact, comparable with the differences arising amongst the several methods available for deducing the accepted values.

(5) *Thermal expansion.*

Certain of the thermal properties of solids will now be examined in the light of the present hypothesis. It is desirable in the first place to form a mental picture of what may be supposed to happen as heat energy is gradually added. Starting at zero temperature, the atoms have no motion and exist in very stable equilibrium in a condition corresponding to the point P in fig. 5, at which $R=A$ and $\frac{dR}{dx}$ considerably exceeds $\frac{dA}{dx}$, thus conferring their stability to the atoms. If momentum is imparted to the atoms a vibratory state is set up and the centre distance r now fluctuates about its mean value r_0 , while the forces of repulsion and attraction vary accordingly up and down the curves about the point P. Owing to the unsymmetrical form of the curves the excursion of the atoms in the positive direction, *i. e.*, increasing centre distance, must exceed that in the negative direction, as already mentioned in the preceding section. The positive and negative excursions, ON and ON' of fig. 7, are determined by the condition that the potential energy of the atom, given by the areas MON and M'ON', shall be equal at the two rest positions of the atom. It is clear from fig. 7 that the difference between ON and ON' increases progressively with the energy possessed by the atom. Any concrete piece of a solid is an aggregation of a very great number of atoms, and at any and every instant all possible values of the fluctuating centre distance are occurring, and consequently the average value must now exceed the original value r_0 at zero temperature, and the linear dimension of the body must be increased to the same extent. We shall therefore assume that if T is the midway point between N and N', then OT is the mean increment in the atomic centre distance, or is the proportional linear expansion of the solid at the temperature corresponding to the atomic energy MON.

It is possible to derive a complete relationship between the proportional expansion, found in the above manner, and the amount of heat energy possessed per atom. Unfortunately the types of function assumed fundamentally for the repulsion and attraction do not lend themselves to algebraic development. On the other hand, it is a straightforward, if laborious, process to allot a series of values to ON and compute arithmetically the values of ONM and from this ON' , and this has been done for a series of metals from the constants previously given in Table VI. of Part I. The results are shown graphically by the group of curves in

Fig. 8.

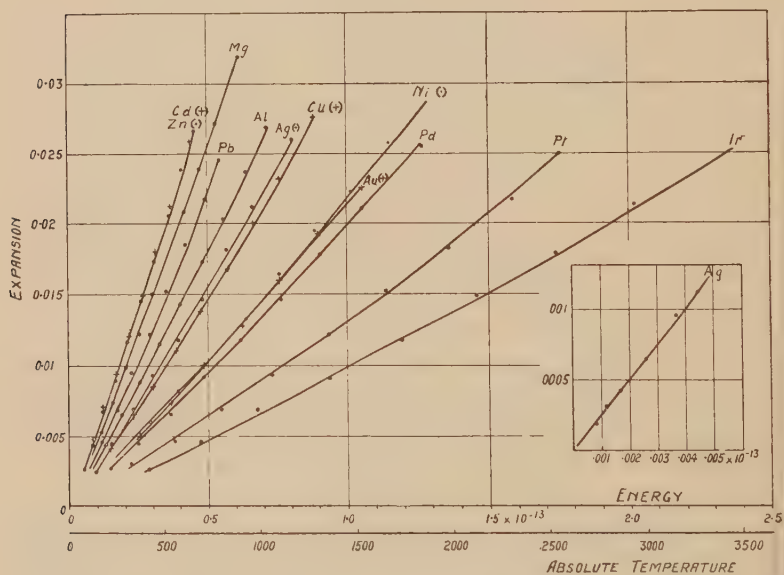


fig. 8. These curves, deduced directly from hypothetical laws of atomic attraction and repulsion, have certain rather remarkable features when considered in relation to the observed thermal properties of the different metals.

It will be assumed that the characteristic stability of a solid vanishes when the atoms are so far apart that $\frac{dR}{dx} = \frac{dA}{dx}$, and hence that when the energy is increased to a point at which the excursion of the atom carries it to such a distance from its neighbour the melting-point is reached. In each case, therefore, the last point on the curve is calculated for

the critical value of ON for which $\frac{dR}{dx} = \frac{dA}{dx}$, the energy being the area OQP in fig. 7.

The first feature of fig. 8 to be noticed is that in every case the theoretical curve relating expansion with energy is nearly a straight line through the origin, indicating that the expansion is nearly proportional to the energy, with a tendency to increase slightly more rapidly than the energy at higher temperatures. If we compare this with experimental observations a close agreement is found to exist. It is well known that the ratio of the coefficient of expansion α to the specific heat σ of the metals is nearly constant over the whole range of temperature that has been explored, with a slight tendency in general to increase with the temperature. Table VIII. gives the ratio $\frac{\alpha}{\sigma}$ at a series of different temperatures for a group of metals⁽²⁾.

This table will be sufficient to show that the constancy of α/σ is a significant property. It is clearly not an incidental result such as would arise if both α and σ were each more nearly independent of temperature. As the table shows, α falls considerably as the temperature is reduced, and the quantum theory of specific heat, supported by Nernst's observations of specific heats at extremely low temperatures, shows that σ actually approaches zero as the temperature is decreased towards zero. It is an interesting feature of the present theory that it should conform so closely with the observed fact that α/σ is constant, and at the same time it indicates that this proportionality continues at temperatures below the limit at present reached in coefficient of expansion determinations. The relation between expansion and energy for silver has been calculated for very low values of the energy, and is shown on a more open scale by the inset curve of fig. 8. This curve shows no tendency to depart from approximate proportionality. This theoretical result implies that the coefficient of expansion also tends to zero at zero temperature.

It is worth while to consider the indications of the theory as regards this point a little further, for it is possible to demonstrate the tendency of the coefficient of expansion to approach zero without any reference to the known similar tendency of the specific heat. Thus in fig. 9 two curves are plotted showing (A) the calculated values of OT of fig. 7 as a function of ON, or expansion against vibration amplitude, and (B) the ratio $\frac{OT}{ON}$ against ON. The momentum of the

atom is proportional to its vibration amplitude, and curve B in particular shows that the ratio of the expansion to the momentum falls continuously as the amplitude diminishes.

TABLE VIII.

Metal.	Temp. C.	α .	$\frac{\alpha}{\sigma}$.
Aluminium	-173	13.6×10^{-6}	0.000107
	-100	18.2	0.00109
	0	23.0	0.00110
	100	24.9	0.00112
	300	29.0	0.00119
	438	29.9	0.00112
Nickel	- 87	10.1	0.000117
	0	12.5	0.00120
	100	14.0	0.00121
	300	16.0	0.00114
	500	16.8	0.00126
Copper	- 87	14.1	0.000174
	0	16.1	0.00177
	100	16.9	0.00180
	400	19.3	0.00179
	600	20.9	0.00182
Silver	-167	15.0	0.000319
	- 87	17.1	0.00329
	0	18.3	0.00327
	100	19.2	0.00331
	500	23.1	0.00350
	800	26.0	0.00342
Platinum	-150	7.4	0.000269
	-100	7.9	0.00268
	0	8.9	0.00280
	100	9.2	0.00277
	875	11.2	0.00267

Thus for an amplitude reduced to a small quantity of the first order the expansion tends to become only a second order quantity.

The next feature of the curves of fig. 8 to be noticed is that the maximum ordinate of each curve is nearly constant

for all the metals. The end point of each curve, as already observed, corresponds to the theoretical melting-point, and the theory therefore leads to the conclusion that the expansion at the melting-point is approximately the same for all the solids concerned. This, again, is a well-known observed fact, sometimes described as Pictet's rule. We can proceed further than this by comparing the actual magnitude of the expansion indicated by the theory with that based on observed data. Table IX. contains the calculated values taken from

Fig. 9.

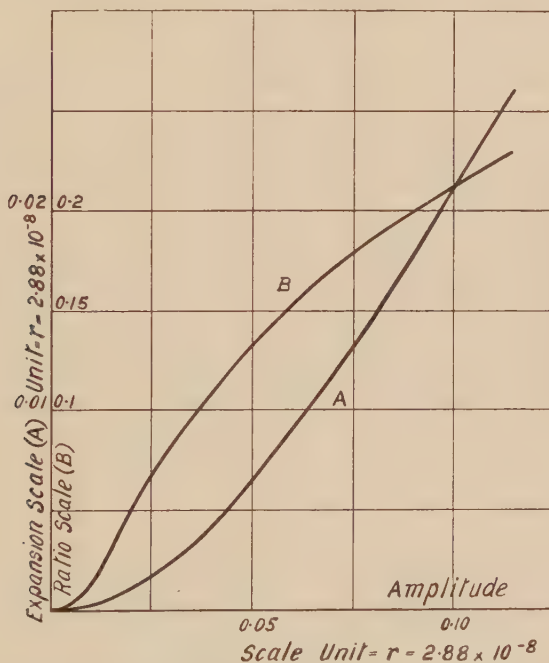


fig. 8, together with the observed values of the product αT_m . In the latter the best mean value has been assigned to the coefficient of expansion α , based on the data given in the International Critical Tables. The temperature interval over which the value of α is averaged is indicated in column 7. The expansion at the melting-point, as deduced from the theory, agrees fairly closely in magnitude with the observed values.

We shall next consider how theoretical values can be calculated separately for the melting-point and the mean

coefficient of expansion. The abscissa of fig. 8 is the mutual energy of a pair of neighbour atoms, denoted by ϵ . In the close-packed lattices each atom has twelve neighbours ; hence the total energy per atom is obtained from ϵ by dividing by 2 and multiplying by 12. If A is the atomic weight of the metal and m is the mass of the oxygen atom the energy per unit mass of the metal is

$$\frac{6\epsilon}{\frac{m}{16}A} = \bar{\sigma}T,$$

where $\bar{\sigma}$ is the mean specific heat from zero to T° .

Hence

$$\epsilon = \frac{mA\bar{\sigma}T}{96} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If we exclude for the present purpose the lowest portion of the temperature scale, we can make use of the result of classical thermodynamics, according to which the atomic heat at constant volume has the value $3R$ for all the mon-atomic elements. The specific heat concerned in equation (7) is the value under constant pressure which exceeds that at constant volume by a small percentage. Further, $\bar{\sigma}$ in the equation is an average value over the whole range of temperature from zero to T , and is known to differ somewhat from the ideal thermodynamic value. Having regard to these approximations, however, we can write equation (7) in the form

$$\epsilon = \frac{mRT}{32}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

an equation showing that the abscissæ of fig. 8 also represent temperature approximately. Taking the mass of the oxygen atom to be 26.34×10^{-24} gm., and the value of R to be 83.15×10^6 in dynamical units, it is found that

$$\epsilon = 6.85 \times 10^{-17} T,$$

and from this relation the temperature scale shown in fig. 8 has been derived.

If the case of silver is taken as an example the maximum expansion has a value 0.0260 and the maximum value of ϵ at the theoretical melting-point is 0.081×10^{-12} erg. The calculated melting-point is therefore

$$T_m = \frac{.081 \times 10^{-12}}{6.85 \times 10^{-17}} = 1181^\circ \text{ abs.},$$

and the mean coefficient of expansion is

$$\alpha = \frac{0.0260}{1181} = 0.000022.$$

These theoretical values can be regarded as comparing quite well with the observed values 1233° abs. and 0.0000187 . A full series of calculated melting-points and coefficients of expansion is given in Table IX. for all the metals which are included in fig. 8. The agreement shown throughout this table between the observed and calculated quantities is quite satisfactory, considering the various causes of uncertainty

TABLE IX.

1.	Total thermal expansion, αT_m .		Melting-point, T_m (abs.).		Coefficient of expansion, α .	
	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.
	2.	3.	4.	5.	6.	7.
					$\times 10^{-6}$	$\times 10^{-6}$
Al ...	0.0269	0.0239	1050	931	25.6	25.7 (-200° to $+600^{\circ}$)
Cu ...	0.0275	0.0254	1295	1356	21.2	18.7 (-200° to $+1000^{\circ}$)
Au ...	0.0227	0.0201	1540	1335	14.75	15.05 (-100° to $+500^{\circ}$)
Ir ...	0.0252	0.0219	3460	2563	7.3	8.54 (-150° to $+1750^{\circ}$)
Pb ...	0.0246	0.0182	800	600	30.7	30.4 (-200° to $+320^{\circ}$)
Ni ...	0.0287	0.0256	1875	1725	15.3	14.85 (-200° to $+1000^{\circ}$)
Pt ...	0.0250	0.0197	2560	1983	9.75	9.95 (-150° to $+1000^{\circ}$)
Ag ...	0.0260	0.0243	1180	1233	22.0	19.7 (-200° to $+900^{\circ}$)
Pd ...	0.0256	0.0242	1850	1822	13.8	13.3 (-200° to $+1000^{\circ}$)
Zn ...	0.0266	0.0229	666	691	39.9	33.2 (-170° to $+300^{\circ}$)
Mg ...	0.0320	0.0253	902	906	35.5	27.9 (-150° to $+500^{\circ}$)
Cd ...	0.0259	0.0176	648	594	40.0	29.7 (-170° to $+200^{\circ}$)

which are present in the calculations. Chief amongst these are the approximate values of the atomic force constants and the approximation involved in the constant 6.85×10^{-17} . The latter is probably responsible for the comparatively wide discrepancy in the melting-points of iridium and platinum.

It is possible to utilize equation (7) in a somewhat different way and compute the mean specific heat σ from the maximum value of ϵ , using for T the known observed value of the melting-point. The mean specific heat of many of the metals is fairly well determined from very low temperatures up to temperatures approaching the melting-points. The results of these calculations are given in Table X., in which the observed mean specific heats are based on data given in

the International Critical Tables and in Landolt and Börnstein's Physical Tables.

The table shows that on the whole the theory yields quite reliable values for the specific heats.

It is worth noticing that in applying the present theory to the thermal properties a much greater range of the atomic forces has been concerned than in the case of the elastic properties. The hypotheses regarding the repulsion and attraction on which the theory is based were derived originally from an examination of the elastic properties, and it is important to find, from the generally good agreement

TABLE X.

	Mean specific heat, $\bar{\sigma}$.	
	Observed.	Calculated.
Al	0.228 (−188° to 600°)	0.248
Cu	0.1048 (−188° to 948°)	0.0895
Au	0.0328 (−188° to 850°)	0.035
Ir	0.0375 (−253° to 1400°)	0.0409
Pb	0.0296 (−253° to 327°)	0.0384
Ni	0.1175 (−253° to 1400°)	0.110
Pt	0.034 (−253° to 1300°)	0.0394
Ag	0.0584 (−253° to 961°)	0.053
Pd	0.0665 (−253° to 1265°)	0.0567
Co	0.131 (−253° to 1187°)	0.111
Zn	0.086 (−253° to 300°)	0.0877
Mg	0.248 (−253° to 615°)	0.0244
Cd	0.0531 (−253° to 321°)	0.0578

obtained with the calculated thermal properties, that the assumed laws of force can bear a great amount of extrapolation beyond the small range covered by elastic phenomena. For example, in the case previously mentioned of silver under a stress of 10,000 lb. per sq. in., the atoms are displaced by only 0.00023 of the distance between them, but at the melting-point the maximum displacement is $0.144r_0$, or nearly 500 times the above elastic displacement.

(6) In the course of the paper it has been shown that most of the physical constants associated with the cohesive properties of solids can be calculated with fair accuracy directly from the atomic forces, the characteristics of which were assumed as the result of previous work. The surmise made at the beginning of the paper, that the cohesive properties

are directly dependent on the properties of the fundamental forces of repulsion and attraction, is thus fully borne out.

Certain known relationships existing between physical properties have been deduced from the theory. These include Pictet's rule, the proportionality between tenacity and elastic modulus, and that between the coefficient of expansion and the specific heat.

The results which have been derived also provide a considerable body of evidence confirming the conclusions reached in Part I. regarding the atomic repulsion. It is made evident, moreover, that the repulsion is the dominating factor in determining the properties of solids. The relatively flexible attraction bond, as its chief function, determines the intrinsic force exerted mutually by adjacent atoms.

It may be premature at present to attempt to find a rational basis for the exponential law of repulsion, but as a purely empirical law it may have a value as a test to be applied to any conceptual model of the atom. In this connexion it is of interest to notice certain general correspondences between the properties of the repulsion derived in this paper and the properties that might be inferred for the new atom model proposed by Sommerfeld, based on Schrödinger's statistical mechanics. This model introduces the conception of an "electron swarm" having spherical symmetry, with a charge density distribution which is a function of the radial distance from the centre. This function varies according to the quantum state, but it is zero at the centre, rising to one or more maxima, and then falling to zero in an exponential manner. If we consider, for simplicity, a positive charge approaching and penetrating such an atom, force will be exerted on the charge (*a*) by the repulsion of the positive nucleus, and (*b*) by the attraction of the negative electron swarm. Both these components will vary relatively slowly until such time as the charge begins to penetrate the electron swarm, when the attraction of the whole shell of electrons outside the charge will be lost. This loss of attraction will be much more rapid than the rate of change of the repulsion of the nucleus, and will therefore contribute the major portion of the total net repulsive effect. Having regard to the exponential distribution of charge density in the outer parts of the spherical swarm of electrons, the net repulsion may also be expected to be approximately an exponential function of the distance of interpenetration, which corresponds with the empirical law deduced in this paper. There are certain other analogous properties of the repulsion of the atom model. Thus the spherical symmetry renders the force of

repulsion independent of direction, a feature strongly suggested by the observed properties of matter. Also the repulsion may readily reach extremely high values, almost without limit, and so provide for the condition obtaining in high-speed gaseous collisions.

It would be exceeding the intended scope of this paper to pursue further these tentative conjectures, which are really in the domain of the mathematician. They perhaps deserve a brief mention as indicating a possible direction in which the exponential law may acquire a rational foundation.

The author, in conclusion, wishes to express his thanks to Sir J. E. Petavel, Director of the N.P.L., for his approval and encouragement of the scheme of re-search of which this paper forms a part. He also acknowledges with thanks the continued and helpful interest of Mr. J. E. Sears, Superintendent of the Metrology Department. He is indebted, also, to Mr. G. D. Preston and Dr. G. Shearer for valuable criticisms and suggestions.

References.

- (1) Lewis, 'Physical Chemistry,' vol. iii. chap. 3.
- (2) 'The Dictionary of Applied Physics.'

LXXXVIII. *Remarks on some Publications of Ramsauer and of Franck and Jordan.* By V. A. BAILEY, M.A., D.Phil., Associate Professor of Physics, University of Sydney*.

THE mean free paths of electrons in gases have been investigated by different methods, and a very complete account of the principal researches on diatomic gases has been given in the *Annalen der Physik* by Brose and Saayman†. Other accounts of the work done on this subject have been given by physicists who have adopted methods of investigation similar to those used by Ramsauer, but they do not include a description of the investigations which were made by Townsend's method, which was first used at the Electrical Laboratory, Oxford. Ramsauer, in a note which appeared recently in the *Annalen der Physik*‡, criticises the account of the investigations of the mean free paths given by Brose and Saayman, and expresses his objections to Townsend's method of investigation. He admits that their account of the work is historically correct, but he

* Communicated by the Author.

† *Ann. d. Phys.* (5) v. pp. 797-852 (1930).

‡ C. Ramsauer, *Ann. d. Phys.* (5) vi. p. 903 (1930).

considers that they have not emphasized the most important point in judging the position. He informs us that in his opinion the results obtained at the Electrical Laboratory, Oxford, are not convincing, but that they receive importance from the fact that he obtains similar results by another method, which he describes as a direct method.

He finds that Townsend's method of determining the mean free path is indirect, and that it involves great mathematical difficulties, and these objections, combined with the fact that Franck and Jordan consider this method to be very indirect, have led him to conclude that the results are unconvincing.

As I have collaborated with Professor Townsend in a large part of this work at Oxford, and have also made other investigations at Sydney based on similar general principles, I may be permitted to point out some facts in connexion with these investigations which have been overlooked by Ramsauer and Franck and Jordan.

With regard to the views expressed by Ramsauer as to the value of indirect methods of investigation, or as to what constitutes a direct method, it is plain that scientists would disagree with him.

Physicists frequently use indirect methods of arriving at conclusions which are generally considered to be satisfactory. For example, the method of finding the mean velocity of agitation of molecules from observations of the pressure and density of a gas is generally accepted. Our method of finding the mean energy of agitation is based on similar considerations depending on the partial pressure of the electrons. It would be quite unscientific to maintain that one of these methods is right and the other wrong, or that they should be rejected on account of mathematical difficulties. Also, if our method of finding the mean free path of an electron is to be considered unconvincing, then the method of finding the mean free path of a molecule from the viscosity of the gas should also be considered to be unconvincing.

In general the formulæ involving mean free paths which are commonly used are approximations, but the formula that occurs in our investigations to find the mean free path of an electron from the coefficient of diffusion is much more easily obtained than the formula for the mean free path of a molecule in terms of the viscosity.

Ramsauer does not appear to be aware of this. He mentions his experiments with argon, which were made at the same time as ours, as illustrating his argument. He found that electrons moving with a certain velocity had a mean free path seven times as long as the gas kinetic value.

This conclusion would be of little value if we accepted his objections to indirect investigations, which must necessarily apply to determinations of the gas kinetic value. It may also be pointed out that several formulæ have been given by mathematicians for the mean free path of a molecule in terms of the viscosity of a gas, but the specification of a collision in these calculations is not the same as that required to explain Ramsauer's observations.

The mean free path is a mathematical quantity which depends on the specification of a collision, and the specification of a collision which was adopted in Townsend's formulæ is substantially the same as the specification of a collision between two molecules in the theory of viscosity or between a molecule of one gas and a molecule of another gas in the theory of interdiffusion of two gases. In fact the formula for the coefficient of diffusion of electrons in terms of the mean free path may be obtained from the formulæ for the coefficient of interdiffusion of two gases.

For this reason our measurements of the mean free paths of electrons, when compared with the mean free paths of molecules derived from experiments on viscosity or on interdiffusion of gases, indicate in a striking manner the difference between the effects of collisions of electrons with molecules and the effects of collisions between molecules.

Many of the well-known properties of ions and electrons were first discovered by these experiments on diffusion, and it would be unreasonable to suppose that the investigations of the mean free paths of electrons are less reliable than the investigation of the diffusion of ions. The fact that the charges on negative ions in all gases are the same as the charge on a monovalent ion in a liquid electrolyte was first shown by the determinations of the coefficients of diffusion of ions in gases at high pressures*. The relation between the charges was subsequently investigated by measuring the lateral diffusion of a stream of ions moving in a uniform electric field through a gas at low pressure†.

These experiments were very simple, and they showed that the charges were the same to a high degree of accuracy. These results may be taken as indicating the accuracy which may be obtained in determining the energy of agitation of the electrons, as the same apparatus is used in each case and the conclusions are obtained from the same theory.

In order to determine the effects of collisions on the motion of the electrons it is necessary to find the velocity of the

* J. S. Townsend, *Phil. Trans. A*, cxcii. p. 129 (1899).

† J. S. Townsend, *Proc. Roy. Soc. A*, lxxx. p. 207 (1908).

electrons in the direction of the electric force as well as the lateral diffusion. The measurements of the velocity were made with the same apparatus, and the results which led to the determinations of the mean free paths have also led to other results which have been accepted by the majority of physicists.

The first experiments from which it was concluded that slow electrons lose only a small proportion of their energy in collisions with molecules were those made at the Electrical Laboratory, Oxford*, which gave the energy of agitation of the electrons.

Pidduck† has shown how the coefficient of restitution may be found from the velocity of agitation and the velocity in the direction of the electric force. It should be mentioned that he was the first to give a quantitative estimate of the degree of elasticity in collisions of electrons with molecules of a gas. The values of the coefficient of restitution e for the collisions of electrons with molecules of air are obtained from the values which he gave for the quantity $f = \frac{1}{2}(1 + e)$. These values of f , corresponding to three different velocities of the electrons, are given in the following table.

The values of k , which is proportional to the mean energy of agitation of the electrons, are given in the first row of the table‡.

k	1.9	21	56
$f = \frac{1}{2}(1 + e)$	0.9993	0.9988	.99

Many writers on this subject do not refer to these investigations, and they are reluctant to say anything about the more recent investigations with monatomic gases. Franck and Jordan, for example, in their book 'Anregung von Quantumsprüngen durch Stöße,' § merely say ||: "In a very indirect way Townsend and Bailey have calculated effective cross-sections from their experiments on lateral diffusion of electrons in an electric field. The results agree only in part with those obtained by the methods already mentioned. Theory and experiment are not suitable for discussion in the scheme of this book."

* J. S. Townsend, Proc. Roy. Soc. A, lxxxi. p. 464 (1908).

† F. B. Pidduck, Proc. Roy. Soc. A, lxxviii. p. 296 (1913); and Proc. Lond. Math. Soc. xv. p. 89 (1915).

‡ $k/27$ is the energy expressed in volts.

§ Julius Springer, 1926.

|| Passage in inverted commas is a translation of the German.

For the development of their theory they find it necessary to show that the collisions of slow electrons with atoms of monatomic gases resemble those between perfectly elastic spheres, and they bring to bear on this problem information gathered from various sources. They reject the first method given by Hertz for calculating the amount of energy lost by electrons in collisions with atoms, and adopt a second theory also published by Hertz. The latter includes a formula for the diffusion of electrons in a field of electric force which is original only in so far as losses of energy of electrons in collisions with molecules are neglected. The experiments on which Franck and Jordan rely are those on the determination of the mean free path by Ramsauer's method and the experiments on the conductivity of helium which were made by Benade and Compton. From these results they obtain the following solution of the problem.

If E be the kinetic energy of an electron, and $\lambda.E$ the amount of energy lost in a collision with an atom of helium, then λ lies between the values 3×10^{-4} and 8×10^{-4} . At the same time they qualify this estimate by pointing out several sources of error in their assumptions, and conclude that one can therefore in the best cases expect only an agreement in order of magnitude between the values of λ calculated from empirical data and the theoretical value 2.9×10^{-4} . This procedure on the part of authors who urge objections against *very indirect* methods is surprising.

There is a remarkable contrast between the attempt made by Franck and Jordan to show that the collisions are perfectly elastic and the results of our experiments * on helium which were published in 1923.

The results we obtained with this gas are given in the following table:—

E	·066	·08	·14	·42	2·0	3·0
$\lambda \times 10^4$	1·3	1·6	2·3	2·5	2·4	2·6
$\lambda_t \times 10^4$	1·2	1·5	2·0	2·5	2·7	2·7

The values of the mean energy E of the electrons (expressed in volts) are given in the first row of the table, the values of λ obtained from the experiments are given in the second row, and the theoretical values λ_t are given in the third row.

* J. S. Townsend and V. A. Bailey, *Phil. Mag.* xlv. p. 657 (1923).

The formulæ for λ_t derived from Pidduck's investigation is

$$\lambda_t = \frac{2m}{M} \left(1 - \frac{E_0}{E} \right),$$

where m is the mass of the electron, M the mass, and E_0 the mean energy of agitation of a molecule of the gas. The value of λ_t diminishes as the energy of agitation of the electrons approaches the energy of agitation of the molecules of the gas. It is therefore not a constant 2.9×10^{-4} as stated by Franck and Jordan.

LXXXIX. *On Oberbeck's Vortices.* By SUDHANSU KUMAR BANERJI, D.Sc., and RAGHUNATH VINAYAK BARAVE, M.Sc.*

[Plates XII. & XIII.]

1. INTRODUCTION.

THE simplest method of generating a vortex is by ejecting a small quantity of fluid into another still fluid. In a remarkable paper published in 1877, Oberbeck † described, in illustration of discontinuous motion in liquids, the beautiful phenomena observed when a coloured water-jet is projected vertically upwards in still water. Both he as well as Reusch ‡, who also observed liquid-vortices by a similar method, coloured the entire liquid, and they were therefore unable to separate out the different stream-lines and thus enter into the details of their mechanism. The diagrams given by Oberbeck show, however, clearly that the flowing liquid develops spiral movements. In recent years, after the classical experiments of Osborne Reynolds, the phenomena of turbulent motion have received considerable attention. Dr. Prandtl § and his students have studied in great detail the turbulent motion behind solid bodies moving in fluid. Many of the photographs given by them show that the stream-lines in the unstable layer behind bodies moving in a fluid have spiral forms, which gradually wind up and ultimately develop into closed

* Communicated by the Authors.

† *Ann. der Phys. und Chem.* ii. pp. 1-16 (1877).

‡ Poggendorf's *Ann.* cx. pp. 399-316 (1860).

§ *Naturwissenschaften*, xiii. pp. 93, 1050 (1925); *Handb. der Phys.* Bd. vii. p. 241 (1927); see also N.P.L. Reports and Bairstow's 'Applied Aerodynamics,' pp. 343-350.

vortices. It does not appear that much attention has been given to the nature of the motion involved in this peculiar type of vortices.

In the present paper we have discussed the mechanism of the vortices involving spiral movements produced by Oberbeck's method. We have also given a hydrodynamical analysis of the motion which explains all the essential features observed. As the coloured liquid has always a slightly different specific gravity from the colourless liquid, we, in our experiments, adopted horizontal ejection with a view to avoiding mostly, if not completely, the complications introduced by gravity.

When repeating Oberbeck's experiments we observed that the vortices were very sensitive to their mode of production. It was found extremely difficult to reproduce the same vortex twice. It was therefore obvious that, for detailed study of the mechanism and properties of a vortex of a particular type during the course of its development, it should be produced by automatic ejection, under the same conditions. Consequently, an automatic arrangement was introduced into the apparatus which enabled us to produce a vortex of a particular type any number of times. It was also considered necessary to colour the ejected liquid in such a way that the colouring matter traced an individual stream-line in the moving liquid and thus revealed the internal structure. Ordinarily the upper and the lower parts of the ejected fluid were coloured, and these, by tracing the boundary stream-lines, disclosed many important features in the development of vortices of this kind. To bring out these features, stationary photographs were taken in the different stages of motion. The translational and rotational speeds involved in the motion were studied by taking moving-film photographs with an arrangement for recording time.

The essential features of the motion are briefly as follows :—

(i.) There are three distinct stages in the life-history of the vortex. The first stage is a stage of development under the influence of the boundary. The second one is a stage of independent development in which the influence of the boundary ceases to operate. The third stage is one in which the stream-lines assume a closed form, and ends in its dissolution.

(ii.) In the first stage the stream-lines, on emergence from the tube, bend outwards and gradually develop spiral

forms called the "head," in which the number of convolutions increases with distance, and this is followed by a "tail." The cessation of the influence of the boundary is marked by the beginning of a contraction of the stream-lines in the end of the "tail."

(iii.) Even after the influence of the boundary has ceased to operate, the convolutions in the spiral structure of the vortex go on increasing until a more or less steady state is reached. This marks the second stage of the motion.

(iv.) In the third stage the spiral stream-lines get closed up and the moving liquid assumes the form of an anchor-shaped vortex.

When the number of convolutions is plotted against the distance of the centre of moving liquid from the edge of the issuing tube, it is noticed that the curve has two points of inflexion almost coinciding with the terminations of the first and second stages.

These and many other important properties, such as the dependence of the structure on the quantity of liquid ejected, the pressure head, and the diameter of the issuing tube, have been discussed in the present paper.

Our thanks are due to Prof. G. R. Paranjpe for the helpful interest he has taken in this investigation.

2. EXPERIMENTAL ARRANGEMENT.

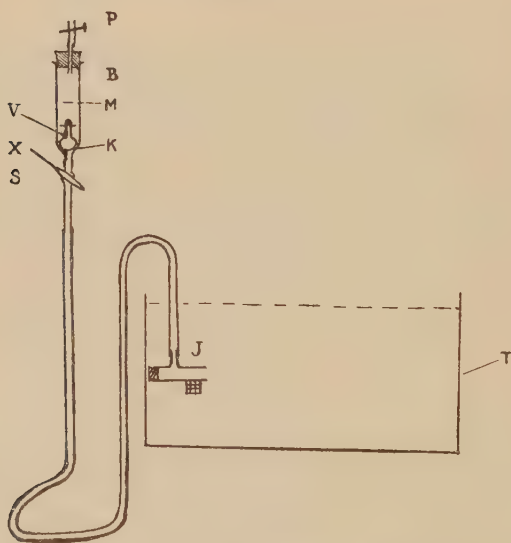
The essential consideration which guided us in deciding our experimental arrangement was that it should be capable of reproducing the same kind of vortex any number of times. Preliminary experiments with Oberbeck's original apparatus, so remarkable for its simplicity, suggested that the chief factors which control the production of the vortices are the "quantity" of the liquid ejected and the time taken by the liquid to come out of the tube. These two factors therefore required to be controlled, and this was attained by introducing slight modification into the original apparatus of Oberbeck. The experimental arrangement adopted by us is shown in fig. 1.

B is a barrel of a wide glass tube with a pinchcock arrangement at the top. At the lower end is a valve V light enough to float in water. It makes a watertight joint at K and works vertically upwards. The barrel, with these attachments, is connected by a small rubber tubing to the stopcock S, which is again joined by a long rubber tubing

to the horizontal glass tube J. This tube is kept dipped into the tank T sufficiently away from all boundary influence. To the stopcock S an index $\bar{X}$ is attached to ensure equal opening during the different experiments.

The whole tube-system is filled with water up to a mark M on the barrel B, and by means of a small bent pipette two streaks of different colours, one slightly heavier and the other slightly lighter than the fluid, are introduced into the tube so that the lighter streak remains clinging to its upper side and the heavier to the lower side. This was

Fig. 1.



the procedure ordinarily adopted for tracing the boundary stream-lines, but occasionally stream-lines in other parts of the jet were also traced by introducing a capillary channel filled with ink at some specified part of the ejecting tube, and allowing the stream to drag the ink along. The capillary channel was found, however, to have a disturbing influence, and furnished very little additional information. An ammoniacal solution of alizarin was found to be the best colouring matter owing to its poor solubility in water, but ordinary fuchsine also served quite well. By working the pinchcock P a definite quantity of the fluid under definite pressure is allowed to emerge through the horizontal tube. Any further and superfluous flow of the fluid is stopped

by the valve when the liquid in the barrel has fallen to a certain point. The apparatus would thus eject a specific quantity under a specified head any number of times, and thus reproduce the same kind of vortex repeatedly.

As it is essential for successful results that the fluid in the tank remains as little disturbed as possible, the subsequent refilling of the barrel, etc., was always done after closing the stopcock S. The barrel was always filled up slightly above the mark to compensate for the loss of "head" which occurs when the pinchcock P is kept closed, but the stopcock S is opened and communication is restored with the tank. A long time was allowed to elapse between two consecutive ejections to enable the disturbed liquid in the tank to come to rest.

The ejected liquid possesses translational as well as rotational motion. The former was studied photographically by a cinematographic camera with an arrangement for recording time on the film itself at regular intervals. This was done by attaching a light paper flag to the pendulum of a metronome and so arranging its position that it would come into the field of the camera only when it oscillated to one extreme end of its excursion. From the measurement of the displacement of the vortices and the time as shown on the records the space-time curves could be easily determined.

The camera gives a photograph of a longitudinal section of the vortex-ring as depicted by the coloured stream-lines. But in the cinematographic films, owing to the smallness of the pictures, the vortices appeared as mere dots, and furnished no details of their structure. It was, consequently, necessary to take stationary photographs of the same size as the original vortices during their movements. For this purpose the same type of vortex was produced under identical conditions repeatedly and instantaneous photographs were taken at different stages of their motion with an exposure of 0.02 second. A calibrated scale placed below the tube was also photographed along with them. The moving-film pictures gave the relationship between distance and time and the stationary photographs the relationship between the change of form and distance, and thus afforded all the materials for the study of the motion involved in the vortices.

It will be shown presently that the factors which determine the character of the motion are:—

- (1) The pressure under which the liquid is ejected.

(2) The quantity of the liquid ejected.

(3) The diameter of the ejecting tube.

The apparatus permits the variation of these factors one at a time, and thus enables us to determine their exact influence on the motion.

3. NATURE OF THE MOTION REVEALED BY STREAM-LINES.

To facilitate the subsequent discussion of the liquid vortices, we shall describe here briefly the essential features of the motion in a typical case, namely, when a definite quantity, about 6 c.c. of water, is ejected through a tube of 1.5 cm. diameter under a pressure of 14 cm., the liquid being coloured at two opposite ends. The movement of the ejected liquid makes the coloured end trace two boundary stream-lines in a longitudinal section through the axis of the jet.

The colour-traces at first come out along the side of the tube and bend outwards. Immediately afterwards they wind up into two small "specks" or "poles," as shown in figs. 1 and 2 of Pl. XII. The specks then force their way through the still liquid and at the same time revolve round themselves in the form of a growing spiral (figs. 3, 4, 5, 6, and 7, Pl. XII.). If we denote the angle of rotation by θ from an axis through the pole of the spiral parallel to the axis of the jet, then when $\theta = 2\pi$ the spiral has developed one "convolution." As the spiral advances through the liquid the number of convolutions goes on increasing, and this is shown by the increasing values of θ .

We shall call the rotating part of the ejected fluid the "head," and the liquid following it, and included between the boundary stream-lines as defined by the colour-traces, the "tail." As the head advances, the "tail" shrinks more and more, the stream-lines come closer and closer, and finally converge almost into a single line (fig. 7, Pl. XII.). The first stage of the motion terminates as soon as the shrinkage of the "tail" begins. In the first stage the number of convolutions shows more or less a progressive increase; in the second stage, which begins as soon as the shrinkage of the tail commences, this rate of increase is not maintained, but undergoes a gradual diminution until a more or less steady state is reached. Throughout the motion the distance between the poles remains practically constant, and, as a

result of the increase in the number of convolutions, the spiral systems round the two poles come closer and closer, and finally the head assumes a rather cloudy appearance and becomes transformed into an anchor-shaped vortex ring in which the spirals are apparently replaced by circular stream-lines. This marks the transition into the third stage.

When a lightly-coloured liquid is ejected, the edges being deeply coloured as before and photographed, it is seen that the moving liquid advances with a definite front, presenting what is picturesquely described by Reusch as a "mushroom formation." The boundary stream-lines reveal the internal motion involved in it (figs. 1, 2, 3, and 4, Pl. XIII.) If arrangement is not made as indicated above for tracing the boundary stream-lines it is not possible to obtain any knowledge of the liquid-motion involved in this interesting type of vortex. This is precisely the reason why Reusch and others, who observed the phenomena with the ejected fluid fully coloured, and without any arrangement for tracing the stream-lines, failed to observe its mechanism.

It is perhaps worth mentioning here that the whole of the ejected liquid does not move forward. The front advances all right; but, owing to the mutual action between the still liquid and the moving head, slices from the rear of the head just outside the "tail" lag behind. This will be clear from figs. 1, 2, and 3 of Pl. XIII. Figs. 1 and 2 show a considerable amount of the coloured liquid round the coiling stream-lines; but, as the head advances, this goes on diminishing, and when the position shown in fig. 3 is reached there is very little coloured liquid round the spirals. This process obviously cannot continue for a long time, for very soon the remaining liquid itself is completely absorbed into the vortex system, which moves forward. Fig. 4 of Pl. XIII. illustrates the mechanism when a similar quantity of liquid is ejected under very low pressure.

The phenomena just described depend on the under-mentioned factors:—

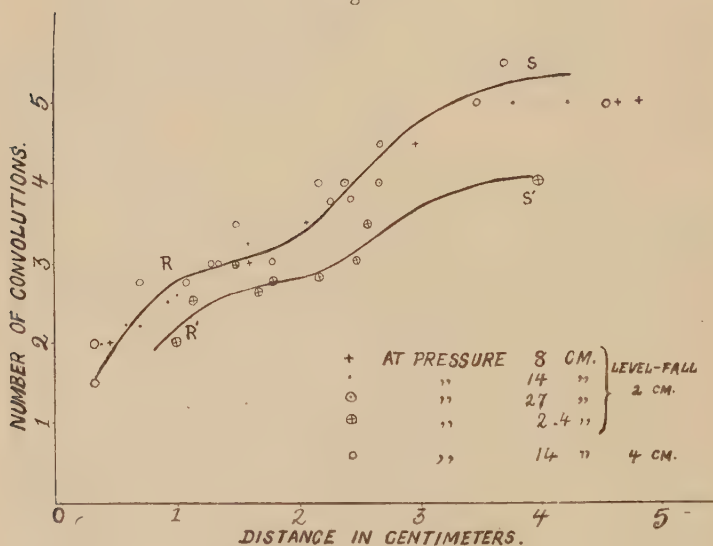
- (1) Pressure under which the liquid is ejected.
- (2) The quantity of the liquid ejected.
- (3) The diameter of the tube.

We shall proceed now to describe the changes in the form of the vortex structure when any of these factors is varied.

4. VORTEX FORMS AND PRESSURE HEAD.

The following typical experiments explain in a general way the manner in which the pressure determines the subsequent motion. In these experiments the diameter of the jet was, as before, 1.5 cm., and the quantity of liquid ejected was about 6 c.c., but the pressures were varied from 8 to 27 cm. It was observed that the velocity of the "head" increased when the pressure was increased. With the movement of the head the "tail" contracted, as explained before, but the suddenness with which the contraction occurred was found to increase with the increase of pressure from 8 to 27 cm.

Fig. 2.



(a) Rotational Motion.

It has already been remarked that, as the "head" moves forward, the number of convolutions increases in the first and the second stage of the motion. This relationship does not appear to depend on the pressure used except when it is very low. The number of convolutions at different distances from the tube for various pressures is shown in Table I. When the number of convolutions is plotted against distance it is noticed that all the points for the pressures 8 to 27 cm. lie evenly about the upper curve in fig. 2.

TABLE I.

Pressure 8 cm. Level-fall 2 cm.		Pressure 14 cm. Level-fall 2 cm.		Pressure 27 cm. Level-fall 2 cm.		Pressure 14 cm. Level-fall 4 cm.		Pressure 2.4 cm. Level-fall 2 cm.	
Distance from the tube in cm.	No. of convolutions.	Distance from the tube in cm.	No. of convolutions.	Distance from the tube in cm.	No. of convolutions.	Distance from the tube in cm.	No. of convolutions.	Distance from the tube in cm.	No. of convolutions.
0.47	2	0.36	2	0.7	2.75	0.35	1.5	0.75	2
0.48	2	0.60	2.25	1.1	2.7	0.35	2	1.1	2.5
1.61	3.25	0.70	2.25	1.3	3.00	1.35	3	1.5	3.0
1.61	3.00	0.95	2.50	2.2	4.00	1.8	3	1.7	2.6
2.12	3.50	1.48	2.50	2.4	4.00	2.3	3.75	1.8	2.75
3.0	4.50	1.95	3.00	2.7	4.00	2.4	3.75	2.2	2.8
4.68	5.00	2.40	4.00	2.7	4.50	2.71	4.5	2.6	3.5
4.83	5.00	3.81	5.00	3.5	5.75	3.5	5	4.0	4.0
		4.27	5.00	3.7	5.50	4.62	5		

But when the pressure is very low, of the order of 2.4 cm., the points representing the number of convolutions with distance are systematically lower than the above series of points, and are best represented by the lower curve in fig. 2. Both curves are very similar in shape, and come closer and closer as they approach the origin where they meet with each other.

The distance-convolution curve appears to be related in an interesting manner with the growth of the vortex structure. In the first stage, which is defined by the portions OR, OR' of the curves in fig. 2, there is a rapid increase in the number of convolutions, and the "tail" does not show any contraction. At the point R or R' the contraction begins, and is followed by a point of inflexion on the curve. So long as the process continues the rate of increase in the number of convolutions is very slow; but as soon as the contraction has been almost completed, the rate of increase in the number of convolutions again becomes large, until the end of the second stage is reached, which is shown by a second point of inflexion on the curve (S or S'). After this a more or less steady condition is attained.

(b) *Translational Motion.*

In order to get an idea of the translational motion of the "head" and its variations, space-time curves for the "head" were obtained, as already explained, by cinematographic methods for various pressure-heads, keeping the diameter of the tube, as well as the quantities of liquid ejected, the same for all of them. For each case two different sets of observations were taken, and it was found that the points given by both lie on the same curve, showing that the vortices produced in the two experiments were almost identical. The curves A, B, C, and D given in fig. 3 represent the relationship between the time and distance of the head from the mouth of the tube for pressures 8, 14, 27, and 39 cm. respectively. In all these cases the ejected liquid was 6 c.c. and the jet 1.5 cm. in diameter. The points given by two independent observations have been shown by dots and circles on each curve. The curves obtained for different pressures, unlike the distance-convolution curves, show small continuous curvature in spite of the changes that occurred in the vortex forms. They are distinct from one another, and their inclination to the time-axis increases as the pressure is increased. They suggest that the velocity of the head undergoes a very slow diminution with time. The

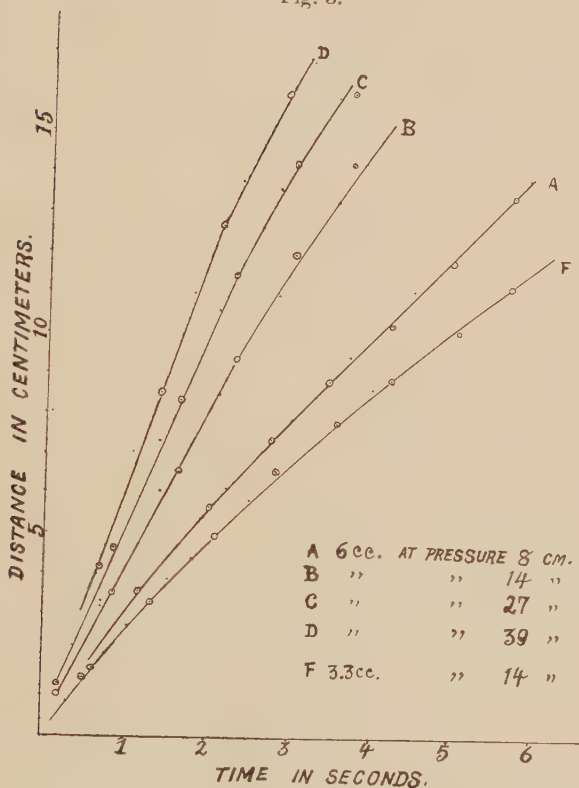
mathematical equations of these curves can be very easily obtained by the method of least squares. The equations for the curves B, C, and D (fig. 3) obtained by this method are given below :—

For B, $S = 4.04 t - 0.064 t^2$.

„ C, $S = 5.72 t - 0.329 t^2$.

„ D, $S = 6.52 t - 0.337 t^2$.

Fig. 3.



In these expressions S represents the distance from the mouth of the tube and t the time expressed in C.G.S. units.

These equations show that the initial velocity of the head when 6 c.c. of liquid is ejected through a tube of 1.5 cm. diameter is 4.04 cm./sec. when the pressure is 14 cm., it is 5.72 cm./sec. when the pressure is 27 cm., and 6.52 cm./sec. when the pressure is 39 cm.

The progressive increase with increase in pressure in the inclination of the curves to the time axis indicates that the translational velocity undergoes an increase, though not at a uniform rate. The above figures, however, suggest that as usual in jets the initial velocity of the head varies almost as the square root of the pressure.

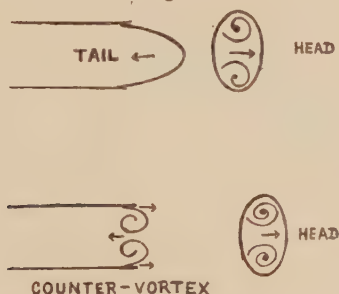
The curve F in fig. 3 represents the distance-time law when a smaller quantity of liquid than those in the above examples, namely, 3.3 c.c., is ejected under a pressure of 14 cm. This curve may be compared with curve B, which also represents a case of ejection under the same pressure and through the same tube. It will be noticed that the translational velocity is smaller in F than in B. Since in these two experiments nothing else is changed except the quantity, and since the momentum per unit quantity is the same in both the cases, the linear velocity should be the same in both if the rotational and the translational momenta be supposed to bear a constant ratio to each other. We find, however, in every case that there is a decrease of translational velocity with decrease in the quantity of the liquid ejected, the other conditions remaining the same. Now the contribution of the vortex to the translational velocity because of its intrinsic linear velocity can very well be neglected, it being very small. It would therefore appear that the ratio of the two momenta is by no means constant in the different cases, not even in the initial stages of the motion. The decrease in the translational velocity when the quantity is decreased must therefore be due to a proportionately larger contribution of momentum per unit quantity for the production of rotational motion. The difference in the distribution of momentum per unit quantity for the production of rotational and translational motions in the different cases would thus appear to be influenced by the "boundary," and not by the factors which give rise to the momentum.

5. CHANGES IN THE VORTEX STRUCTURE WHEN THE QUANTITY OF LIQUID EJECTED IS VARIED.

We have seen that when the pressure is not very low and generally exceeds 8 cm. the number of convolutions at any particular distance is almost independent of pressure provided the other factors remain unaltered. We can therefore work with any pressure exceeding 8 cm. to determine the manner in which the quantity of liquid affects the structure of the vortex. The case when a very small

quantity of liquid is ejected is very interesting. It was observed that when 1.5 c.c. of liquid is ejected through a tube of 1.5 cm. diameter the "tail" breaks up somewhere in its middle and coils back into the tube, thus generating what may be called a "counter-vortex" (Pl. XIII. fig. 5). The translational and rotational motions involved in the counter-vortex appear to be quite the opposite of those of the head. The counter-vortex phenomenon, however, does not present itself when the quantities ejected are large, namely, 6 c.c. and above. Since the counter-vortex appears only when the quantity of liquid ejected is very small, an explanation is to be sought from the fact that the quantity ejected is insufficient for the maintenance of a continuous flow for an appreciable time, and consequently there is almost an impulsive separation

Fig. 4.



of the head from the tail. The head moves forward and the tail backwards, as in the familiar example of shot and gun. The diagrams in fig. 4 explain the process.

Another important feature noticed when small quantities of liquid are ejected is that the diameter of the head, *i. e.*, the distance between the two poles, decreases as soon as the "tail" breaks. When the liquid ejected lies between 6 c.c. and 12 c.c., the phenomena observed are already described in art. 3. When the quantity is increased to 12 c.c. and above, the two boundary lines in the "tail" lose their stream-line appearance and become diffused (Pl. XIII. fig. 6).

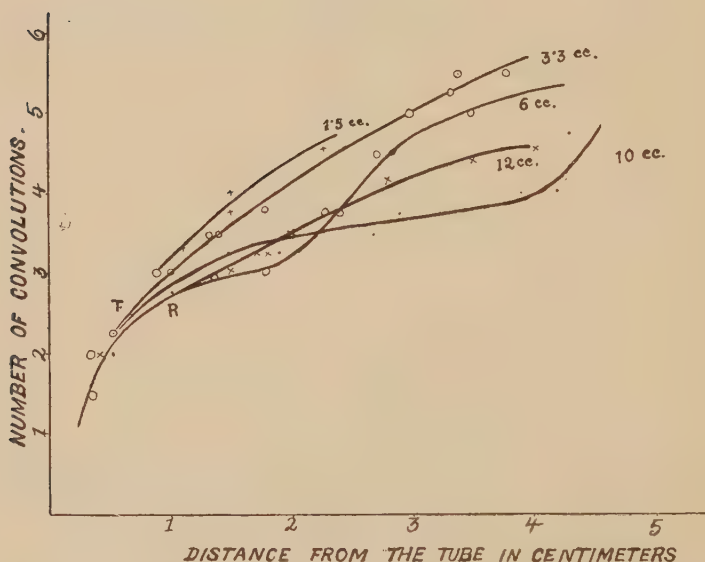
For pressures within the range investigated, *viz.*, 8 to 27 cm., distance-convolution curves were obtained for different quantities of the ejected liquid, keeping the diameter of the tube unaltered. The quantities ejected were 1.5 c.c., 3.3 c.c., 6 c.c., 10 c.c., and 12 c.c., and the

respective convolution-distance curves have been shown in fig. 5.

It will be seen that the curves for 1.5 c.c. and 3.3 c.c. proceed with a continuous curvature. The curve for 6 c.c. shows two points of inflexion, that for 10 c.c. only one, and that for 12 c.c. none again.

As stated before, each of these points of inflexion corresponds to a structural change. The beginning of the flatness associated with the first point of inflexion just corresponds with the beginning of the contraction of the

Fig. 5.



“tail,” and the end of the flatness with the termination of the contraction. The period during which the curve remains flat coincides with a gradual narrowing of the “tail.” As soon as the maximum contraction has occurred the inclination of the curve again increases, suggesting an increase in the rate of increase of convolutions. The second point of inflexion appears in the case of the curve for 6 c.c. just when the cloudy appearance, as described in art. 3, begins immediately before the transition into the closed anchor-shaped vortex. All the curves approach very near each other at about the point R, and eventually meet at the origin. The number of convolutions in this part of the

first stage increases rapidly with distance, and is almost independent of the ejected quantities. Since all the other factors were varied, except the diameter of the tube, we may assume roughly that in this stage the growth in the number of convolutions is determined by the diameter of the tube.

The curves show that the points of inflexion are not appreciably marked when the quantities ejected are so small as 1.5 c.c. or 3.3 c.c.; but they become quite conspicuous when the quantities ejected are 6 c.c. and 10 c.c. They become again inappreciable when the quantities ejected are 12 c.c. or more. It is thus seen that the points of inflexion become pronounced in the intermediate range when the quantities ejected lie between 6 c.c. and 10 c.c. (about).

The reason for this appears to be that when the quantities ejected are small the period during which the contraction of the tail occurs covers only a short distance. The change of curvature associated with the first point of inflexion should therefore occur within a very narrow limit, roughly between the origin and the point marked **T** on the curves. The change of curvature, if any, under such circumstances must be extremely small. Lack of observational points, as well as the limit of accuracy of the observations do not permit any such change of curvature to be established within such a small compass.

The non-appearance of the first point of inflexion when the quantities ejected are 12 c.c. and above may be associated with the fact that no contraction of the "tail" is seen to occur when such large quantities are ejected.

In those cases which do not show the second points of inflexion the cloudy appearance mentioned before does not occur at all, and the transformation to the closed vortex ring is produced straightway.

6. INFLUENCE OF THE BOUNDARY.

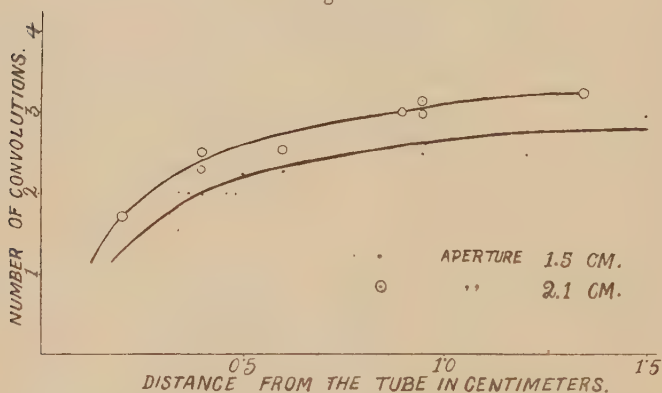
For the same quantity of liquid ejected, under the same pressure, it does not appear that there is much change in the structure of the "head" when the diameter of the tube is varied. The velocity of the "head" is decreased when the diameter of the tube is increased. This suggests that the momentum per unit aperture is the quantity that primarily controls the subsequent behaviour of the ejected liquid through a circular tube.

In the last article it is shown that the first stage of motion is, to a large extent, controlled by the boundary of the

tube. To find out whether the dimensions of the boundary play any part in the subsequent development of the moving liquid in this stage observations with two different tubes having the diameters 1.5 cm. and 2.1 cm. were made.

The number of convolutions in the first stage has been plotted against distance for these two cases in fig. 6. It is seen that the curves are very similar to each other and run almost parallel, suggesting that the dimensions of the boundary have definite influence on the growth of the vortex in this stage. Since the curves must necessarily meet at the origin, it is clear that the tube of larger diameter contributes to a more rapid growth of the convolutions in the early stage. This would agree with the observed fact stated above, that the translational velocity is smaller in the case

Fig. 6.



of the tube of larger diameter. The momentum per unit quantity at the time of emergence being the same in both the cases, the reduction in the translational momentum in the case of the tube of larger diameter must necessarily be accompanied by an increase in the rotational momentum.

7. MATHEMATICAL THEORY.

The two-dimensional *irrotational* motion of a liquid flowing out from a canal bounded by two thin parallel walls into an open space was given by Helmholtz * in the form

$$z = -w + e^{-w}, \quad (1)$$

where

$$z = x + iy$$

and

$$w = \phi + i\psi,$$

* Lamb's 'Hydrodynamics,' fourth edition, p. 71.

x and y being the rectangular coordinates of a point and ϕ and ψ the velocity potential and stream function respectively.

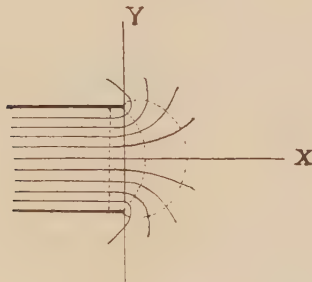
We get

$$\left. \begin{aligned} x &= -\phi + e^{-\phi} \cos \psi, \\ y &= -\psi - e^{-\phi} \sin \psi. \end{aligned} \right\} \cdot \cdot \cdot \cdot (2)$$

The stream-lines and the equipotential curves as given by these equations are shown in the diagram given below (fig. 7).

In the case under consideration water is ejected horizontally through a tube not into open space, but into water. The motion is not two-dimensional. When, however, we compare the motion in any section through the axis of

Fig. 7.



the tube, we notice that the motion when the liquid just emerges from the tube (as represented in fig. 1 of Pl. XIII.) shows a close similarity with that represented in the above diagram. We would therefore assume that the initial state of the motion in any section can be represented by expressions of the form given above.

We notice that the expression for z given above consists of two terms, $-w$ and e^{-w} . Now $z = -w$ merely represents the straight stream-lines and straight equipotential lines *inside* the tube, while $z = e^{-w}$ represents the effect on these stream-lines and equipotential lines in consequence of the emergence of the jet into open space. The term $z = -w$ gives a constant velocity to the jet throughout the motion. Neglecting this constant velocity, which can be superposed whenever we desire, we see that in the case under consideration the velocity potential and the stream function

representing the *initial state* of the motion just outside the tube are given by

$$\phi + i\psi = -\log(x + iy). \quad . \quad . \quad . \quad . \quad (3)$$

We shall now show that if we do not restrict ourselves to the limitation that the motion is irrotational, and, further, if we take viscosity into consideration, then the streamlines in the fluid issuing out of a tube into a medium formed of the same fluid must assume spiral forms.

Owing to symmetry we can consider the motion in any section through the axis of the tube as two-dimensional.

We therefore start with the ordinary equations of hydrodynamics for movements in one plane, namely

$$\left. \begin{aligned} \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} &= X - \frac{1}{\rho} \frac{\partial p}{\partial x}, \\ \frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} &= Y - \frac{1}{\rho} \frac{\partial p}{\partial y}. \end{aligned} \right\} \quad . \quad . \quad . \quad (4)$$

The accelerating forces whose components are X and Y must consist of two terms, the first arising on account of the fact that the motion involves rotation and the second on account of friction, the liquid being viscous.

The rotation in the liquid introduces a force whose components have the forms

$$X_1 = -\lambda v, \quad Y_1 = \lambda u, \quad . \quad . \quad . \quad . \quad (5)$$

where 2λ denotes the angular velocity at any point round an axis parallel to the axis of Z .

We shall assume the viscous resistance to the motion of liquid to be proportional to velocity, and to be expressible in the form

$$X_2 = -\mu u, \quad Y = -\mu v. \quad . \quad . \quad . \quad . \quad (6)$$

The factor μ is dependent on the nature of the liquid. By introducing these forces in the equation of motion, we obtain

$$\left. \begin{aligned} \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} &= -\lambda v - \mu u - \frac{1}{\rho} \frac{\partial p}{\partial x}, \\ \frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} &= \lambda u - \mu v - \frac{1}{\rho} \frac{\partial p}{\partial y}. \end{aligned} \right\} \quad . \quad . \quad (7)$$

If, as usual, we denote the angular velocity of an element round an instantaneous axis parallel to the axis of Z by 2ζ , we have

$$\zeta = \frac{\partial u}{\partial y} - \frac{\partial v}{\partial x}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The equations (7) can be written in the form

$$\left. \begin{aligned} \frac{\partial}{\partial x} \left\{ \frac{p}{\rho} + \frac{1}{2}(u^2 + v^2) \right\} + \frac{\partial u}{\partial t} + \mu u &= -(\lambda + \zeta)v, \\ \frac{\partial}{\partial y} \left\{ \frac{p}{\rho} + \frac{1}{2}(u^2 + v^2) \right\} + \frac{\partial v}{\partial t} + \mu v &= (\lambda + \zeta)u. \end{aligned} \right\} \quad (9)$$

It is thus clear that the introduction of the angular velocity 2ζ has merely the effect of increasing λ to $\lambda + \zeta$ in the above hydrodynamical equations. Having, therefore, taken account of the rotations in the force terms, we can assume $\zeta = 0$, or

$$\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x} = 0. \quad \dots \dots \dots (10)$$

We now write

$$\left. \begin{aligned} u &= Ue^{-\alpha t}, \quad v = Ve^{-\alpha t}, \\ \frac{p}{\rho} + \frac{1}{2}(u^2 + v^2) &= Pe^{-\alpha t}, \end{aligned} \right\} \dots \dots \dots (11)$$

and

where α is a constant and U, V are independent of t . When expressed in this form P is not and cannot be independent of t . The equations (9) now reduce to the forms

$$\left. \begin{aligned} \frac{\partial P}{\partial x} + (\mu - \alpha)U &= -\lambda V, \\ \frac{\partial P}{\partial y} + (\mu - \alpha)V &= \lambda U. \end{aligned} \right\} \dots \dots \dots (12)$$

We proceed to solve these equations on the assumption that at any instant λ is uniform throughout the moving liquid. The solution thus obtained will be rigorously true over those regions where this condition is strictly satisfied. We write

$$U = \frac{\partial \phi}{\partial x} + \frac{\partial \psi}{\partial y}, \quad V = \frac{\partial \phi}{\partial y} - \frac{\partial \psi}{\partial x}, \quad \dots \dots (13)$$

and put

$$\left. \begin{aligned} L &= P + (\mu - \alpha)\phi - \lambda\psi, \\ M &= (\mu - \alpha)\psi + \lambda\phi. \end{aligned} \right\} \dots \dots \dots (14)$$

We thus obtain

$$\frac{\partial L}{\partial x} + \frac{\partial M}{\partial y} = 0, \quad \frac{\partial L}{\partial y} - \frac{\partial M}{\partial x} = 0. \quad \dots \dots \dots (15)$$

These equations are satisfied if

$$L = f(t) \quad \text{and} \quad M = \text{constant}.$$

The second equation of (14) therefore gives

$$\psi = -\frac{\lambda}{\mu - \alpha} \phi, \quad . \quad . \quad . \quad . \quad (16)$$

in which an arbitrary constant has been omitted. Then from the first of these equations we get

$$P = f(t) - (\mu - \alpha) \phi \left\{ 1 + \frac{\lambda^2}{(\mu - \alpha)^2} \right\}. \quad . \quad . \quad (17)$$

The components of velocity are given by

$$\left. \begin{aligned} u &= Ue^{-\alpha t} = \left(\frac{\partial \phi}{\partial x} - \frac{\lambda}{\mu - \alpha} \frac{\partial \phi}{\partial y} \right) e^{-\alpha t}, \\ v &= Ve^{-\alpha t} = \left(\frac{\partial \phi}{\partial y} + \frac{\lambda}{\mu - \alpha} \frac{\partial \phi}{\partial x} \right) e^{-\alpha t}. \end{aligned} \right\} \quad . \quad . \quad (18)$$

The resultant velocity q is given by

$$\begin{aligned} q^2 = u^2 + v^2 &= \left\{ \left(\frac{\partial \phi}{\partial x} \right)^2 + \left(\frac{\partial \phi}{\partial y} \right)^2 \right\} \\ &\times \left\{ 1 + \frac{\lambda^2}{(\mu - \alpha)^2} \right\} e^{-2\alpha t}, \quad . \quad . \quad . \quad (19) \end{aligned}$$

and the pressure p is given by

$$\begin{aligned} \frac{p}{\rho} &= \left[f(t) - (\mu - \alpha) \phi \left\{ 1 + \frac{\lambda^2}{(\mu - \alpha)^2} \right\} \right] e^{-\alpha t} \\ &- \frac{1}{2} \left\{ \left(\frac{\partial \phi}{\partial x} \right)^2 + \left(\frac{\partial \phi}{\partial y} \right)^2 \right\} \left\{ 1 + \frac{\lambda^2}{(\mu - \alpha)^2} \right\} e^{-2\alpha t}. \quad (20) \end{aligned}$$

All the quantities are thus expressed in terms of a single unknown function ϕ . If the liquid is regarded as incompressible, the equation of continuity gives $\nabla^2 \phi = 0$. In consequence of equation (10) or (16) ψ also satisfies the equation $\nabla^2 \psi = 0$. We can therefore write

$$\phi + i\psi = F(x + iy), \quad . \quad . \quad . \quad (21)$$

which gives

$$\frac{\partial \phi}{\partial x} = \frac{\partial \psi}{\partial y} \quad \text{and} \quad \frac{\partial \phi}{\partial y} = -\frac{\partial \psi}{\partial x}. \quad . \quad . \quad (22)$$

The differential equation of the stream-lines is

$$u dy = v dx,$$

or

$$\begin{aligned} \frac{\lambda}{\mu - \alpha} \left\{ \frac{\partial \phi}{\partial x} dx + \frac{\partial \phi}{\partial y} dy \right\} &= \frac{\partial \phi}{\partial x} dy - \frac{\partial \phi}{\partial y} dx \\ &= \frac{\partial \psi}{\partial y} dy + \frac{\partial \psi}{\partial x} dx. \end{aligned}$$

The stream-lines are therefore given by

$$\psi - \frac{\lambda}{\mu - \alpha} \phi = \text{constant.} \quad . \quad . \quad . \quad . \quad (23)$$

The stream-lines therefore intersect the system of lines, $\phi = \text{constant}$, at an angle which is the same everywhere. If we denote by ϵ the angle which the direction of the stream-lines makes with the normal to the curves $\phi = \text{constant}$, then we have

$$\tan \epsilon = \frac{\lambda}{\mu - \alpha}. \quad . \quad . \quad . \quad . \quad (24)$$

We see from equation (3) that, on the assumption that the motion inside the tube is irrotational, the functions ϕ and ψ in the initial stage, just on emergence of the liquid from the tube, satisfy the relation

$$\phi + i\psi = \log (x + iy).$$

This being the initial condition, which determines the subsequent motion, we can consider that ϕ and ψ continue to satisfy a relation of this kind even when rotation and viscosity are introduced in the hydrodynamical equations. With a suitable choice of axes the relation between ϕ and ψ in general for the motion under consideration will be of the type

$$\phi + i\psi = \log \{ (x - a) + i(y - b) \}, \quad . \quad . \quad (25)$$

where a, b are two constants depending on the position of the origin of coordinates chosen. Using polar co-ordinates with respect to an origin at the point (a, b) , we can put

$$\left. \begin{aligned} x - a &= r \cos \theta, \\ y - b &= r \sin \theta. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (26)$$

We thus get

$$\phi = \log r, \quad \psi = \theta. \quad . \quad . \quad . \quad . \quad (27)$$

Equation (23) shows that the stream-lines are equiangular spirals having the equation

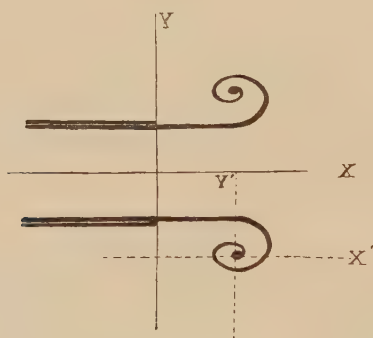
$$\theta - \frac{\lambda}{\mu - \alpha} \log r = \text{constant},$$

or $r = A e^{\theta \cot \epsilon}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$

where A is a constant.

If the coordinate axes are taken as shown in fig. 7, the stream-lines at any instant will be a series of equiangular spirals. The observed stream-lines are of the type shown in fig. 8, and closely approximate to the equiangular spirals. It is seen that a, b represent the coordinates of the pole of the spirals. Owing to symmetry the motion in three dimensions can be pictured by rotating the spirals about the axis of the tube.

Fig. 8.



The radius of curvature of the equiangular spiral is $r \operatorname{cosec} \epsilon$, and since the observation shows that the curvature of the spiral actually described by the stream-lines is large, ϵ must be very nearly equal to $\frac{\pi}{2}$. Equation (24) therefore shows that $\frac{\lambda}{(\mu - \alpha)}$ is large. In other words, α is very nearly equal to μ . Equations (18) and (27) give the components of velocity in the form

$$\left. \begin{aligned} u &= \left\{ (x-a) - \frac{\lambda}{\mu - \alpha} (y-b) \right\} \frac{1}{r^2} e^{-at}, \\ v &= \left\{ (y-b) + \frac{\lambda}{\mu - \alpha} (x-a) \right\} \frac{1}{r^2} e^{-at}. \end{aligned} \right\} \quad . \quad (29)$$

We notice that the first term within the brackets in each of the above expressions is contributed by the translational motion, and the second term by the rotational motion.

The resultant velocity q is given by

$$q^2 = u^2 + v^2 = \left\{ 1 + \frac{\lambda^2}{(\mu - \alpha)^2} \right\} \cdot \frac{1}{r^2} e^{-2\alpha t}.$$

Therefore

$$q = \frac{C}{r} e^{-\alpha t},$$

where

$$C = \pm \left\{ 1 + \frac{\lambda^2}{(\mu - \alpha)^2} \right\}^{\frac{1}{2}} \cdot \cdot \cdot \cdot \quad (30)$$

We thus see that at any instant the velocity at a point varies inversely as its distance from the pole of the spiral. This is the law which governs the motion in the well-known type of vortex defined by the relationship "velocity $\times$ distance = constant."

If ω is the angular velocity round the pole, then, since the curvature of the spiral is very large and it very nearly approaches a circular vortex, we have approximately

$$\omega = \frac{q}{r} = \frac{C}{r^2} e^{-\alpha t},$$

or

$$\frac{d\theta}{dt} = \frac{C}{r^2} e^{-\alpha t} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (31)$$

That is to say

$$\int r^2 d\theta = C \int e^{-\alpha t} dt,$$

or

$$A^2 \int e^{2\theta \cot \epsilon} d\theta = C \int e^{-\alpha t} dt.$$

Integrating, we get

$$\frac{A^2}{2 \cot \epsilon} e^{2\theta \cot \epsilon} = -\frac{C}{\alpha} e^{-\alpha t} + \text{constant}.$$

If time is reckoned from the instant when the liquid just emerges from the tube, we have $\theta = 0$ when $t = 0$. Therefore

$$\frac{A^2}{2 \cot \epsilon} (1 - e^{2\theta \cot \epsilon}) = -\frac{C}{\alpha} (1 - e^{-\alpha t}). \quad \cdot \cdot \cdot \quad (32)$$

Since ϵ is very nearly equal to $\frac{\pi}{2}$, $\cot \epsilon$ is small, and since α is very nearly equal to μ it is also small. Consequently, as a first approximation, we have from the above equation

$$\frac{A^2}{2 \cot \epsilon} \times 2\theta \cot \epsilon = -\frac{C}{\alpha} \times \alpha t,$$

$$\text{or} \quad \theta = -\frac{C}{A^2} t. \quad . \quad . \quad . \quad . \quad . \quad (33)$$

It will be seen from equation (30) that C may be either positive or negative. For the upper spiral in fig. 8 C is positive, and for the lower spiral C is negative. Since "convolution" is proportional to θ , we see from this equation that the number of convolutions will increase with time in agreement with the observed results. The process which makes the number of convolutions increase with time cannot, however, continue indefinitely. After a stage of development the spiral must close up and be transformed into a circular vortex of the type mentioned above, as is, indeed, shown by the experiments.

We have seen in the experiments that the pole moves almost parallel to the x -axis. If, then, we transfer the origin to a point on the edge of the tube, and denote by $(x, 0)$ the coordinates of the pole at any instant, we see from equation (30) that the motion of translation of the pole will be given by

$$\frac{dx}{dt} = \frac{C}{x} e^{-\alpha t}.$$

Therefore

$$\int x dx = C \int e^{-\alpha t} dt,$$

$$\text{or} \quad \frac{1}{2} x^2 = -\frac{C}{\alpha} e^{-\alpha t} + \text{constant},$$

$$\text{or} \quad x^2 = \frac{2C}{\alpha} (1 - e^{-\alpha t}), \quad . \quad . \quad . \quad . \quad . \quad (34)$$

if time is reckoned from the instant the liquid emerges out of the tube.

The distance-time curves for the motion of the pole obtained experimentally and shown in fig. 3 are exactly of the type represented by the analytical equation given above.

Since α is small, these curves are to a first approximation given by equations of the type

$$x^2 = 2Ct; \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

that is to say, they are approximately parabolas, having the time axis as their axis. We have already shown that $\lambda/(\mu - \alpha)$ is very large, and consequently from equation (30) it will be seen that C is also very large. These parabolas have therefore very large *latera recta* exactly agreeing with the observed results.

8. SUMMARY.

The detailed structure of the liquid-vortices produced by Oberbeck's experiments has been studied in this paper. An automatic arrangement was introduced into the apparatus, so that the same vortex could be reproduced any number of times. The stream-lines in the moving liquid were traced by colouring its specific parts, and these were photographed at various stages of the motion. The space-time relationship was obtained by cinematographic films with an arrangement for recording time. A longitudinal section of the moving liquid shows that the stream-lines have the form of a double-spiral advancing through the liquid and at the same time presenting an increased number of convolutions, and followed by a "tail." The "tail" contracts, and after a time the spirals close up, and the moving liquid is transformed to an anchor-shaped vortex and is finally dissipated away. It appears that there are three distinct stages in the life-history of the vortex. In the first stage it is under the influence of the tube, in the second stage it is freely developing uninfluenced by the boundary, and in the third stage it transforms itself into an anchor-shaped vortex and meets with dissolution. Each of these stages is associated with a distinct change in the structure and the rotational motion of the vortex. These have been studied in detail in this paper. A mathematical theory has been given which explains the essential features of the motion.

Colaba Observatory, Bombay.

July 10, 1930.

XC. A Modified Equation for the Heats of Dilution of Solutions of Strong Electrolytes. By OLIVER GATTY.*

WHEN building up the charge on an ion in solution the work may be regarded as being done partly against the electric fields of the other ions and partly against the field of the ion itself. Debye⁽¹⁾ assumed that for dilute solutions the work required for the latter process was independent of the concentration, and so, by considering an isothermal process in which all the ions were discharged simultaneously, he obtained an expression for the electric work of dilution which reduces in the case of very small ions to

$$\Delta W = -\frac{\sum N_i z_i^2 \epsilon^2}{3D} \kappa, \quad \dots \dots \dots (i.)$$

where

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \frac{\sum N_i z_i^2}{V} \quad \dots \dots \dots (ii.)$$

and $\frac{1}{\kappa}$ is the radius of the ionic atmosphere, the solution has a total volume V , and contains $N_1 \dots N_i \dots N_r$ particles of sorts $1 \dots i \dots r$ carrying charges $z_1\epsilon \dots z_i\epsilon \dots z_r\epsilon$; D denotes the dielectric constant of the solvent, " $-\epsilon$ " the charge on an electron, ΔW the evolution of electric work that would accompany the addition of an infinite bulk of solvent to the solution, and k is Boltzmann's constant. Should the isothermal process of charging the ions take place at constant volume, ΔW on general thermodynamic grounds would represent the increase (in this case a negative one) of the work function A of the system ($A = E - TS$ in the notation of G. N. Lewis⁽²⁾).

If the process of charging the ions takes place at constant pressure, however, there would be a change in volume owing to electrostriction of the solvent, but the observed values for the change with concentration of the molal volume of electrolytes in dilute solutions show that the alteration in electrostriction with dilution must be very small. This small volume change will only affect the electric contribution to the work of charging the ions by altering the value of V in the expression for κ , so that for solutions more dilute than $N/100$, which are the only solutions for which the simple expression (i.) is expected to hold, the effect of electrostriction will be negligible.

* Communicated by Sir Harold Hartley, F.R.S.

Thus, as Debye⁽¹⁾ has pointed out, ΔW represents the difference between the electric work of charging all the ions at dilution V and at infinite dilution by an isothermal and reversible process either at constant volume or at constant pressure. In the former case ΔW represents the increase in A , but not the increase in the free energy function F for the constant volume process*; while in the latter it represents the increase in F , but not the increase in A , for the constant pressure process. Thus the four quantities A_v , F_v , A_p , F_p are very nearly equal to each other. This is most marked in the case of A_v and F_p , and for dilute solutions they may both be regarded as equal to ΔW .

Bjerrum⁽³⁾ was the first to use expression (i.) to derive the following equation for the heat of dilution U of electrolytes:

$$U = \kappa \cdot \frac{\sum N_i z_i^2 \epsilon^2}{2D} \left(1 + \frac{T}{D} \frac{dD}{dT} \right). \quad \text{. . . . (iii.)}$$

In this expression it is not stated whether $\frac{dD}{dT}$ is $\left(\frac{\partial D}{\partial T} \right)_p$ or $\left(\frac{\partial D}{\partial T} \right)_v$, and it is probable that they are not identical. Furthermore, the dilution of electrolytes may be brought about by adding solvent to the solute under a variety of conditions, and in particular the process of dilution may be made to take place at constant volume or at constant pressure.

Experiments usually involve measurements of $\left(\frac{\partial D}{\partial T} \right)_p$ and of the heat of dilution at constant pressure rather than the corresponding quantities at constant volume. Theoretically the heats of dilution either at constant volume or at constant pressure can be calculated from equations (i.) and (ii.) by the Gibbs-Helmholtz equation as follows:—

$$\left(\frac{\partial \left(\frac{A}{T} \right)}{\partial T} \right)_v = - \frac{E}{T^2}, \quad \text{. (iv. a)}$$

$$\left(\frac{\partial \left(\frac{F}{T} \right)}{\partial T} \right)_p = - \frac{H}{T^2}, \quad \text{. (iv. b)}$$

Now

$$2\kappa \left(\frac{\partial \kappa}{\partial T} \right)_v = \kappa^2 \left[1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_v \right], \quad \text{. (v. a)}$$

* $F = E + pV - TS$ in the notation of G. N. Lewis.

$$\text{and } 2\kappa \left(\frac{\partial \kappa}{\partial T} \right)_p = \frac{\kappa^2}{T} \left[1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_p + \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p \right]. \quad (\text{v. } b)$$

Therefore

$$\begin{aligned} \left(\frac{\partial \left(\frac{\Delta W}{T} \right)}{\partial T} \right)_v &= -\frac{\Delta E}{T^2} = +\kappa \frac{\sum N_i z_i^2 \epsilon^2}{3DT^2} \left[1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_v \right] \\ &\quad + \frac{\sum N_i z_i^2 \epsilon^2}{3DT} \left(\frac{\partial \kappa}{\partial T} \right)_v \\ &= +\kappa \cdot \frac{\sum N_i z_i^2 \epsilon^2}{2DT^2} \left[1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_v \right], \quad (\text{vi. } a) \end{aligned}$$

and similarly

$$\begin{aligned} \left(\frac{\partial \left(\frac{\Delta W}{T} \right)}{\partial T} \right)_p &= -\frac{\Delta H}{T^2} = +\kappa \cdot \frac{\sum N_i z_i^2 \epsilon^2}{2DT^2} \\ &\quad \left[1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_p + \frac{T}{3V} \left(\frac{\partial V}{\partial T} \right)_p \right]. \quad (\text{vi. } b) \end{aligned}$$

Thus, if the difference between the electrical contribution to the internal energy of the solution at dilution V and at infinite dilution is represented by ΔE , and the corresponding difference of the electrical contributions to the total heat content of the solution by ΔH , we may write

$$\Delta E = -\kappa \cdot \frac{\sum N_i z_i^2 \epsilon^2}{2D} \left[1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_v \right], \quad (\text{vii. } a)$$

$$\Delta H = -\kappa \cdot \frac{\sum N_i z_i^2 \epsilon^2}{2D} \left[1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_p + \frac{T}{3V} \left(\frac{\partial V}{\partial T} \right)_p \right]. \quad (\text{vii. } b)$$

The first expression is identical with that given by Bjerrum, referred to constant volume, and the latter differs from it, referred to constant pressure, by the term $\frac{T}{3V} \left(\frac{\partial V}{\partial T} \right)_p$,

which is only a 6.7 per cent. correction in the case of water. This term, however, becomes significant in the case of several non-aqueous solvents, and amounts to a 41.8 per cent. correction in the case of nitromethane, as is shown in Table I.

Equations (iii.) and (vii. b) can both be reduced to the form $V_c = B\sqrt{C}$, where V_c , which is the heat evolved on isothermal mixing of the solution at concentration c with an infinite bulk of the solvent, is the difference between the molar heat of solution at infinite dilution and at concentration c (the

“integral heat of dilution” of Lange)⁽⁷⁾. Thus if L_c denote the molar heat of solution at concentration c

$$V_c = L_o - L_c. \quad \dots \quad \text{(viii.)}$$

If V_c is the heat evolved on mixing, at constant volume, the solution at concentration c with an infinite excess of pure solvent, V_c is the ΔE of equation (vii. *a*), and if it is the heat of mixing at constant pressure V_c is the ΔH of equation

TABLE I.

Solvent.	Dielectric constant D.	Density d .	$1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_p$	$\frac{T}{3V} \left(\frac{\partial V}{\partial T} \right)_p$
Water at 25° C.	78.14	0.99707	-0.379 ⁽⁴⁾ & ⁽⁶⁾	+0.0254
Water at 20° C.	79.97 ⁽⁵⁾	0.99823	-0.356 ⁽⁴⁾	+0.0202
Methyl alcohol at 20° C.	33.16	0.79164	-0.629 ⁽⁴⁾	+0.1162
Ethyl alcohol at 20° C.	23.93	0.78934	-0.889 ⁽⁵⁾	+0.1056
Nitromethane at 20° C.	37.48	1.1373	-0.275 ⁽⁴⁾	+0.1150
Nitrobenzene at 20° C.	35.41	1.2034	-0.540 ⁽⁴⁾	+0.0802

TABLE II.

Solvent.	B from equation (iii.).	B from (vii. <i>b</i>).
Water, 25°	528	492
Water, 20°	483	456
Methyl alcohol, 20°..	3197	2607
Ethyl „ 20°..	7370	6491
Nitromethane, 20° ...	1163	677
Nitrobenzene, 20° ...	2487	2118

(vii. *b*). The values of B calculated for a uni-univalent salt from equations (iii.) and (vii. *b*) are given in Table II., where V_c is expressed in calories per mole and c in moles per 1000 c.c. of solvent.

The value of B found experimentally by Lange and Leighton⁽⁸⁾ for aqueous solutions of KCl at 25° C. is 376, and the correction of 6.7 per cent. is not nearly enough to account for the discrepancy between theory and experiment

in this case, and naturally cannot account for the individual differences in the value of B observed for different salts. However, in the case of nitromethane, methyl alcohol, and ethyl alcohol the additional term will make a considerable difference.

The calculated values for B depend on the experimental values for D and $\frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_p$, and the results of different investigations of the dielectric constant of water show that too much reliance must not be placed on these data. The dielectric constant of ethyl alcohol has recently been measured by Smythe and Stoops⁽⁵⁾, and their values are used in Table I., where the other values are taken from the results of Lattey and Gatty⁽⁴⁾. Even if these figures are only of the right order of magnitude it is evident that it is not justifiable to ignore $\frac{T}{3V} \left(\frac{\partial V}{\partial T} \right)_p$ in the case of methyl alcohol, ethyl alcohol, or nitromethane. In the case of water the correction is smaller than probable errors in B , owing to uncertainties about the dielectric constant, and different salts have individual values for B at 25°C. which are known to vary⁽⁹⁾ from 280 in the case of KNO_3 to 376 in the case of KCl . But it is perhaps significant that the additional term always lessens the discrepancy between experiment and theory for all the values of $\left[1 + \frac{T}{D} \frac{\partial D}{\partial T} \right]$ for water at 25°C quoted by Lange and Robinson⁽⁶⁾ excepting those of Maas (0.142) and of Drude (0.272). The latter gives good agreement for aqueous KCl without the correction. In the case of nitromethane the difference between the two predicted slopes is so great that it should be possible to distinguish experimentally between the two equations in spite of uncertainties about the correct values for D and $\frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_p$ for this solvent. Experiments are already in progress, in this laboratory, and it is hoped that a test of the above equations will shortly be made.

Gronwall, La Mer, and Sandved⁽¹⁰⁾, considering the effect of higher order terms, have produced an improved solution of the original Debye and Hückel equations, which in the notation used in this paper becomes

$$\frac{\Delta W}{kT} = \sum_1^g N_i z_i \sum_{m=1}^{m=\infty} \left(-\frac{\epsilon^2 z_i}{D a_i k T x_i^2} \right)^m \int_0^{x_i} x^{2m-1} \psi_m(x) dx \\ - \sum_1^g \frac{N_i z_i^2 \epsilon^2}{2 D a_i k T} \cdot \cdot \cdot \cdot \cdot \quad (\text{ix.})$$

if we assume that the dielectric constant of the solution is the same as that of the pure solvent. In this equation a_i is the radius or the electrostatic capacity of an ion of sort i , and $x_i = \kappa a_i$, where $\frac{1}{\kappa}$ is the radius of the ionic atmosphere and $\psi_m(a_i x_i)$ a function which can be readily calculated in the case of a simple binary z - z valent electrolyte with the help of tables compiled by Gronwall, La Mer, and Sandved.

Lange and Meixner⁽¹¹⁾ have calculated the heats of dilution of simple z - z valent electrolytes when the ions both have the same radius a and $x = \kappa a$, from these equations by means of the Gibbs-Helmholtz equation with the assumption that $\frac{da}{dT} = 0$ for both ions.

Their equation is

$$V_c = NkT \left(1 + \frac{T}{D} \frac{dD}{dT} \right) \left\{ \sum_{m=0}^{m=\infty} \left(\frac{\epsilon^2 z^2}{D a k T} \right)^{2m+1} X_{2m+1}(x) - \frac{\epsilon^2 z^2}{D a k T} \right\}, \quad (\text{x.})$$

where V_c is expressed in ergs per gram molecule of salt, N is Avogadro's number, $X_{2m+1}(x)$ is obtained from Gronwall's tables, and " a " is the ionic radius of the ions which are assumed to be of the same size.

This equation is either meant to represent ΔE and not ΔH , or else the fact that κ depends on V has been neglected; perhaps deliberately, because the resulting term was assumed to be negligible.

The correction for the higher order equation can be calculated as follows. The Gibbs-Helmholtz equation gives

$$\left(\frac{\partial (\frac{\Delta W}{kT})}{\partial T} \right)_{p, N_1 \dots N_r} = - \frac{\Delta H}{kT^2}, \quad \dots \quad (\text{xi.})$$

and the only variables in ΔW for a solution in which all the N 's are kept constant are T , D , and κ . Under these conditions κ depends on T , D , and V , and therefore one may write

$$\frac{\Delta W}{kT} = f(T, D, V); \quad \dots \quad (\text{xii.})$$

$$\begin{aligned} \therefore - \frac{\Delta H}{kT^2} = & \left[\left(\frac{\partial f}{\partial T} \right)_{DV} + \left(\frac{\partial f}{\partial D} \right)_{VT} \left(\frac{\partial D}{\partial T} \right)_p \right. \\ & \left. + \left(\frac{\partial f}{\partial V} \right)_{TD} \left(\frac{\partial V}{\partial T} \right)_p \right]_{N_1 \dots N_r} \quad \dots \quad (\text{xiii.}) \end{aligned}$$

Lange and Meixner have given equations which correspond to the first two terms on the right in equation (xiii.) if their

$\frac{dD}{dT}$ is replaced by $\left(\frac{\partial D}{\partial T}\right)_p$. Thus the remaining term that has to be added in is

$$-kT^2 \left\{ \frac{\partial \left(\frac{\Delta W}{kT} \right)}{\partial V} \right\}_{TD} \left(\frac{\partial V}{\partial T} \right)_{p, N_1 \dots N_r} \dots \quad (\text{xiv.})$$

Now $\left\{ \frac{\partial \left(\frac{\Delta W}{kT} \right)}{\partial V} \right\}_{TD, N_1 \dots N_r}$ has been used to calculate the osmotic coefficient ϕ , since ΔW is really an "A" term ($A = E - TS$), and has always been regarded as such; thus

$$\left\{ \frac{\partial \left(\frac{\Delta W}{kT} \right)}{\partial V} \right\}_{TD, N_1 \dots N_r} = \frac{(1-\phi) \cdot \Sigma N_i}{V}, \quad \dots \quad (\text{xv.})$$

and the correction to the heats of dilution becomes from (xiv.)

$$- [kT(1-\phi) \Sigma N_i] \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_{p, N_1 \dots N_r} \dots \quad (\text{xvi.})$$

Gronwall, La Mer, and Sandved have shown that for a simple z - z valent salt with both ions of radius a

$$1-\phi = \left\{ \frac{\epsilon^2 z^2}{kTDa} \left[\frac{1}{x} - \frac{1}{2} \cdot \frac{1}{1+x} - \frac{1}{x^2} \log 1+x \right] - \sum_{m=1}^{m=\infty} \left(\frac{\epsilon^2 z^2}{kTDa} \right)^{2m+1} \left[\frac{1}{2} \frac{X(x)}{2m+1} - \frac{2m+1}{2m+1} \frac{Y(x)}{2m+1} \right] \right\}, \quad (\text{xvii.})$$

and they have constructed tables for X_{2m+1} and Y_{2m+1} . So that the expression for $V_c (= \Delta H)$ in ergs per mole of salt in the modified Lange equation becomes

$$V_c = NkT \left(1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right)_p \right) \left\{ \sum_{m=0}^{m=\infty} \left(\frac{\epsilon^2 z^2}{Da kT} \right)^{2m+1} \frac{X(x)}{2m+1} - \frac{\epsilon^2 z^2}{Da kT} \right\} \\ - 2NkT \left(\frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p \right) \left\{ \sum_{m=1}^{m=\infty} \left(\frac{\epsilon^2 z^2}{Da kT} \right)^{2m+1} \left[\frac{2m+1}{2m+1} \frac{Y(x)}{2m+1} - \frac{1}{2} \frac{X(x)}{2m+1} \right] \right\} \\ + \frac{\epsilon^2 z^2}{Da kT} \left[\frac{1}{x} - \frac{1}{2} \cdot \frac{1}{1+x} - \frac{1}{x^2} \log 1+x \right] \dots \quad (\text{xviii.})$$

As a check on equations (xvi.) and (vii. b) it may be noted that on the simplest Debye theory

$$kT(1-\phi) \Sigma N_i = +\kappa \frac{\Sigma N_i z_i^2 \epsilon^2}{6D} = -\frac{\Delta W}{2},$$

and therefore the correction to be applied to equation (iii.) is given by

$$+ \frac{\Delta W T}{2 V} \left(\frac{\partial V}{\partial T} \right)_p = -\kappa \frac{\sum N_i z_i^2 \epsilon^2}{2 D} \left(\frac{T}{3 V} \left(\frac{\partial V}{\partial T} \right)_p \right),$$

in agreement with equation (vii. b).

Summary.

The use of the free energy or constant pressure function (F of G. N. Lewis) leads to the introduction of another term into the equations for heats of dilution of electrolytes. Denoting the osmotic coefficient of the solution by ϕ , this additional term is

$$-(kT(1-\phi)\Sigma N_i) \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p,$$

and for the simplest Debye equations this reduces to

$$\frac{\Delta W}{2} \frac{T}{V} \left(\frac{\partial V}{\partial T} \right)_p = \kappa \frac{\sum N_i z_i^2 \epsilon^2}{2 D} \left(\frac{T}{3 V} \left(\frac{\partial V}{\partial T} \right)_p \right).$$

$\frac{T}{3 V} \left(\frac{\partial V}{\partial T} \right)_p$ is small compared with $\left[1 + \frac{T}{D} \left(\frac{\partial D}{\partial T} \right) \right]_p$ in the case of water, but becomes significant in the case of several non-aqueous solvents.

In conclusion, I would like to thank Sir Harold Hartley for his constant help and advice throughout the course of this work.

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XCI. *An X-Ray Investigation of the Lead-Bismuth and the Tin-Bismuth Alloys.* By D. SOLOMON, B.Sc.(Wales), and W. MORRIS JONES, M.A., M.Sc., F.Inst.P. (Department of Physics, University College of Swansea)*.

INTRODUCTION.

THE following paper gives the results of an X-ray investigation of the lead-bismuth and tin-bismuth alloys, the work being a continuation of that carried out in this laboratory on crystal structures in binary systems. The crystal structures in the copper-antimony⁽¹⁾ and lead-antimony⁽²⁾ alloys have already been determined and some of the results for the tin-antimony⁽³⁾ system have been reported, so it seemed of interest to investigate also the structures in the lead-bismuth and tin-bismuth systems. Further, workers elsewhere have investigated the crystal structures of several other alloys of antimony, but, with the exception of a recent paper on the copper-bismuth⁽⁴⁾ alloys, no analysis seem to have been published for alloys of the similar metal bismuth.

Brady, in his report on the structure of eutectics⁽⁵⁾, has examined the microstructures of an alloy of lead-bismuth and an alloy of tin-bismuth at a eutectic composition, and states that the structures are extremely similar and show an abundance of what have been termed by some "herring-bone" structure. Examination of the microphotographs, however, does not give information as to the ultimate crystalline structures present.

The specific heats of the lead-bismuth and tin-bismuth systems have been determined by O. Richter⁽⁶⁾. The experimental results in the case of the lead-bismuth system differ widely from those calculated by the simple rule of mixtures. This divergence has been explained as due, probably, to the formation of solid solutions, or to the presence in the alloys of a structure different from that of either of the components. The divergence from the simple rule in the case of the tin-bismuth system is not so strongly marked.

The metallurgy of the lead-bismuth system has been the subject of many investigations, the most recent complete work being that of W. Herold in 1920⁽⁷⁾. From

* Communicated by the Authors.

thermal analysis and electrical conductivity measurements he reports that a solid solution exists at the lead end of the equilibrium diagram up to about 22 per cent. by weight of bismuth, and at the bismuth end of about 1 per cent. by weight of lead, these limits being not, however, clearly defined. He finds no other phases or compounds present in the system.

Earlier investigations on the tin-bismuth alloys show evidence of the formation of two compounds, BiSn_2 and Bi_3Sn . More recent work, however, by A. W. Smith ⁽⁸⁾ denies the existence of any compounds in the system, but shows that tin is slightly soluble in bismuth, and bismuth insoluble in tin at room temperature.

Though the two systems under discussion have given rise to much metallurgical investigation, there is still no certainty as regards the constitution of their equilibrium diagrams, and no satisfactory explanation, for instance, as to why the specific heats of the lead-bismuth alloys differ so widely from that expected on the simple rule of mixtures. Thus it was hoped that an analysis of the crystal structures, which are in themselves a fundamental physical property of the alloys, would also give results which would lead to a more complete understanding of other properties and help to remove uncertainties in the equilibrium diagrams.

Method of Experiment.

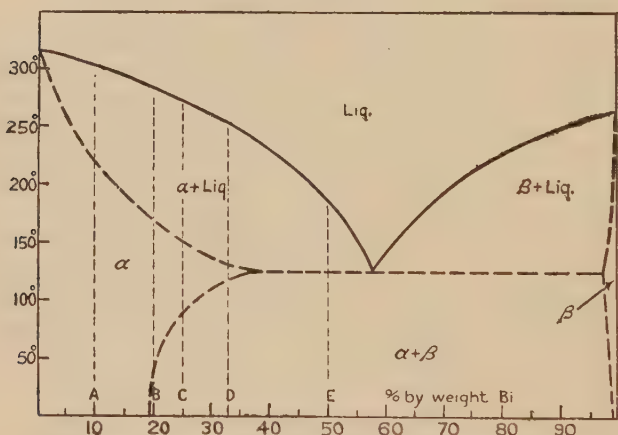
The crystal structures were investigated by the X-ray powder method. The copper target used in the X-ray tube gave rise to two radiations K_α and K_β , the latter being absorbed as far as possible by a thin filter of nickel. As in previous work carried out in this laboratory, a film of NaCl was taken to calibrate the camera and a correction curve drawn by which all subsequent films were corrected. NaCl films were taken at regular intervals to correct for any slight variation in the position of the central rod of the camera. The metallic powder was painted on this rod until the diameter of the rod and powder was between .65 and .75 mm. This was ensured by measurement with a travelling microscope. The calibration of the camera and the accuracy of measuring up the film were checked by taking a powder photograph of copper and comparing the dimensions of the unit cell obtained,

$a_0 = 3.610$ Å.U., with those taken as a standard to-day for this metal, *i. e.*, $a_0 = 3.608 \pm .003$ (Westgren's results). With the precautions taken to ensure accuracy of measurement, a change in the size of a crystal lattice of $\frac{1}{6}$ of 1 per cent. could be detected.

The Lead-Bismuth System.

The equilibrium diagram usually accepted for the lead-bismuth system is that given in the 'International Critical Tables,' vol. ii. and is reproduced in fig. 1, and this

Fig. 1.



Equilibrium diagram of the lead-bismuth system. Dotted verticals indicate compositions investigated.

diagram was taken as the standard for the present work. The dotted verticals on the diagrams have been added to indicate the compositions at which photographs were taken to investigate the crystal structures. In addition, powder photographs were also taken of the end components, lead and bismuth. The compositions of the alloys examined are given in Table I. The alloys were annealed for long periods and allowed to cool very slowly.

Results.

It is well known that lead has a face-centred cubic lattice of side $a_0 = 4.930$ Å.U. The spacings as obtained from measurements on the X-ray powder photograph taken for lead are given in Table II.

TABLE I.

Alloy.	Percentage by weight of lead.	Density.	Type of structure.	Size of cell.
Pure lead	100	11.38	face-centred cubic	$a_0 = 4.930 \text{ \AA. U.}$
A	90	11.27	face-centred cubic	$a_0 = 4.938 \text{ \AA. U.}$
B.....	80	11.19	{ face-centred cubic hexagonal close-packed	$\begin{cases} a_0 = 4.946 \text{ \AA. U.} \\ a_0 = 3.477 \text{ \AA. U.} \end{cases} \quad c = 1.66$
C	75	11.17	hexagonal close-packed	$a_0 = 3.477 \text{ \AA. U.} \quad c = 1.66$
D.....	67	11.14	hexagonal close-packed	$a_0 = 3.483 \text{ \AA. U.} \quad c = 1.66$
E.....	50	10.86	{ hexagonal close-packed face-centred rhombohedral	$\begin{cases} a_0 = 3.483 \text{ \AA. U.} \\ a_0 = 6.540 \text{ \AA. U.} \end{cases} \quad \begin{matrix} c = 1.66 \\ a = 87^\circ 34' \end{matrix}$
Pure bismuth	0	9.82	face-centred rhombohedral	$a_0 = 6.540 \text{ \AA. U.} \quad a = 87^\circ 34'$

This table is inserted in order that the plane spacings of pure lead may be compared with those of alloy A (90

TABLE II.

Radiation.	Plane.	Lead.		
		Intensity.	Observed. d/n .	Calculated. d/n .
K_{α}	111	M.	2.840	2.846
K_{α}	100 ⁽²⁾	M.	2.461	2.465
K_{β}	110 ⁽²⁾	V.W.	1.747	1.743
K_{α}	110 ⁽²⁾	St.	1.742	1.743
K_{α}	131	St.	1.486	1.484
K_{α}	111 ⁽²⁾	M.	1.423	1.423
K_{α}	100 ⁽⁴⁾	W.	1.229	1.232
K_{α}	331	M.	1.130	1.129
K_{α}	120 ⁽²⁾	M.	1.102	1.099
K_{α}	112 ⁽²⁾	M.	1.005	1.006
K_{α}	151	M.	.948	.947
K_{α}	110 ⁽⁴⁾	W.	.870	.871

Structure : Face-centred cubic.

Dimension of unit cell : $a_0 = 4.930 \text{ \AA.U.}$

TABLE III.

Alloy "A." Composition :—90 per cent. lead ; 10 per cent. bismuth (solid solution).

Radiation.	Plane.	Intensity.	Alloy "A."	
			Observed. d/n .	Calculated; d/n .
K_{α}	111	M.	2.837	2.850
K_{α}	100 ⁽²⁾	M.	2.457	2.469
K_{β}	110 ⁽²⁾	V.W.	1.744	1.746
K_{α}	110 ⁽²⁾	St.	1.739	1.746
K_{α}	131	St.	1.484	1.486
K_{α}	111 ⁽²⁾	M.	1.425	1.425
K_{α}	100 ⁽⁴⁾	W.	1.233	1.234
K_{α}	331	M.	1.132	1.131
K_{α}	120 ⁽²⁾	M.	1.100	1.101

Structure : Face-centred cubic.

Dimension of unit cell : $a_0 = 4.938 \text{ \AA.U.}$

per cent. lead, 10 per cent. bismuth). Powder photographs of long exposure were taken of this alloy, and examination

of the films showed that no bismuth lines were present on the photographs. This verifies that the alloy A lies within the region of solid solutions of bismuth in lead. The data for alloy A are given in Table III.

The X-ray analysis shows that the solution of bismuth in lead has produced a small expansion of the lead lattice

TABLE IV.

Alloy "B." Composition :—80 per cent. lead ; 20 per cent. bismuth.

Radiation.	Plane.	Intensity.	Observed. $d/n.$	Calculated. $d/n.$
*K $_{\alpha}$	10 $\bar{1}$ 0	W.	2.998	3.011
K $_{\alpha}$	111	M.	2.831	2.855
*K $_{\alpha}$	10 $\bar{1}$ 1	M.	2.654	2.670
K $_{\alpha}$	100 ⁽²⁾	M.	2.454	2.473
*K $_{\beta}$	10 $\bar{1}$ 2	V.W.	2.080	2.083
*K $_{\alpha}$	10 $\bar{1}$ 2	W.	2.084	2.083
K $_{\beta}$	110 ⁽²⁾	Y.W.	1.728	1.748
K $_{\alpha}$	110 ⁽²⁾	St.	1.743	{ 1.748
*K $_{\alpha}$	11 $\bar{2}$ 0 ⁽²⁾			{ 1.739
*K $_{\alpha}$	10 $\bar{1}$ 3	M.	1.615	1.621
K $_{\alpha}$	131	St.	1.487	{ 1.489
*K $_{\alpha}$	11 $\bar{2}$ 2			{ 1.489
*K $_{\alpha}$	20 $\bar{2}$ 1	V.W.	1.458	1.457
K $_{\alpha}$	111 ⁽²⁾	M.	1.424	1.427
*K $_{\alpha}$	10 $\bar{1}$ 1 ⁽²⁾	V.W.	1.334	1.335
K $_{\alpha}$	100 ⁽⁴⁾	W.	1.236	1.236
*K $_{\alpha}$	20 $\bar{2}$ 3	V.W.	1.185	1.186
K $_{\alpha}$	331	M.	1.133	1.133
*K $_{\alpha}$	12 $\bar{3}$ 1	V.W.	1.118	1.117
K $_{\alpha}$	120 ⁽²⁾	M.	1.104	1.103

Mixture of a face-centred cubic lattice, dimensions $a_0=4.946$ Å.U., and an hexagonal close-packed lattice, dimensions $a_0=3.477$ Å.U., $c=1.66$.

NOTE.—The lines of the hexagonal close-packed lattice are denoted by *.

from 4.930 to 4.938 Å.U. The atomic radii of lead and bismuth are respectively 1.74 and 1.82 Å.U. for co-ordination number 12 (Goldschmidt⁽⁹⁾), and the smallness of the expansion of the lead lattice on the solution of 10 per cent. bismuth is due to the bismuth atom being only slightly larger than the lead atom.

The film taken of alloy B (80 per cent. lead, 20 per cent. bismuth) showed the presence of two crystal structures: one, the face-centred cubic lattice, and the other a hexagonal close-packed lattice. The lines belonging to the hexagonal close-packed lattice were faint and required a long exposure to bring them out, while the lines due to the face-

TABLE V.

Alloy "C." Composition:—75 per cent. lead; 25 per cent. bismuth.

"Alloy "D." Composition:—67 per cent. lead; 33 per cent. bismuth.

Plane.	Intensity.	Alloy "C."		Alloy "D."	
		Observed. d/n .	Calculated. d/n .	Observed. d/n .	Calculated. d/n .
10 $\bar{1}$ 0	M.	3.018	3.011	3.019	3.016
0001 ⁽²⁾	M.	2.872	2.886	2.894	2.891
10 $\bar{1}$ 1	St.	2.680	2.670	2.677	2.674
10 $\bar{1}$ 2	M.	2.081	2.083	2.087	2.086
11 $\bar{2}$ 0 ⁽²⁾	M.	1.747	1.739	1.752	1.742
10 $\bar{1}$ 3	St.	1.621	1.621	1.626	1.624
11 $\bar{2}$ 2	M.	1.489	1.489	1.493	1.493
20 $\bar{2}$ 1	V.W.	1.458	1.457	1.453	1.459
10 $\bar{1}$ 1 ⁽²⁾	W.	1.332	1.335	1.341	1.337
10 $\bar{1}$ 4	W.	1.297	1.301	1.301	1.303
20 $\bar{2}$ 3	W.	1.183	1.186	1.185	1.188
12 $\bar{3}$ 1	W.	1.116	1.117	1.117	1.119
11 $\bar{2}$ 4	W.	1.108	1.110	1.111	1.112
10 $\bar{1}$ 5	W.	1.076	1.078	1.074	1.079

Structure of alloy "C": Hexagonal close-packed.

Dimensions of unit cell $\begin{cases} a_0 = 3.477 \text{ \AA.U.} \\ c = 1.66. \end{cases}$

Structure of alloy "D": Hexagonal close-packed.

Dimensions of unit cell $\begin{cases} a_0 = 3.483 \text{ \AA.U.} \\ c = 1.66. \end{cases}$

centred cubic lattice were strong. This hexagonal lattice was not expected, for the equilibrium diagram indicates that the only structures likely to be present in the alloys should be those of the compound elements. The data from measurements on the film are given in Table IV.

The face-centred cubic spacings in the table are those of an expanded lead lattice of side $a_0 = 4.946 \text{ \AA.U.}$ showing

a further slight expansion of the lattice from that of alloy A. The other set of spacings of the hexagonal close-packed structure gave lattice constants $a_0 = 3.477$ Å.U. and axial ratio $c = 1.66$. This structure was further examined by means of alloys C (75 per cent. lead, 25 per cent. bismuth) and D (67 per cent. lead, 33 per cent. bismuth). The lines on the film for these two alloys were entirely those of the hexagonal structure as found in alloy B, and after long exposure no lines due to lead or bismuth were detected. The data are given in Table V.

An examination of the table shows that the hexagonal structure persists alone from 25 to 33 per cent. of bismuth, and the base of the cell expands from 3.477 to 3.483 Å.U. for this range, the axial ratio remaining constant. The X-ray analysis therefore reveals a phase having a close-packed hexagonal structure existing alone over the range 25 to 33 per cent. of bismuth. The density of alloy "D" is 11.41, and if we take the atomic weight of the mean atom as $\frac{1}{3}(2 \cdot \text{Pb} + \text{Bi}) = 207.5$, then the volume of the unit cell shows that two such atoms are associated with it. The composition of alloy 33 per cent. bismuth can be represented by the chemical formula Pb_2Bi , but if a compound Pb_2Bi were present, the X-ray data should indicate a much larger unit cell than that found, in order that it should contain a whole number of molecules. No evidence indicating the presence of a larger cell was detected. The alloy Pb_2Bi is therefore just a composition in a range of solid solution extending from 25 to 33 per cent. bismuth. The analysis for alloy E, below, indicates that the composition Pb_2Bi is at the limit of this range. Previous metallurgical investigations also show quite definitely that no intermetallic compound is present in this system.

The data for alloy E (50 per cent. lead 50 per cent. bismuth) show that the crystal structures present consist of a mixture of the hexagonal close-packed lattice and the face-centred rhombohedral lattice of bismuth. The spacings for the hexagonal structure are the same as those in alloy D, indicating that the size of the hexagon lattices in these two alloys is the same. As the bismuth lines on the film were also fairly strong, these two facts indicate that from about 33 per cent. bismuth to 100 per cent. bismuth the alloys are a mixture of the close-packed hexagonal and the face-centred rhombohedral phases.

The spacings for the face-centred rhombohedral phase are those of pure bismuth. Herold⁽⁷⁾ states that the solid solution of lead in bismuth is not more than about 1 per cent. by weight. As the atoms of lead and bismuth

TABLE VI.

Alloy "E."

Composition :—50 per cent. lead ; 50 per cent. bismuth.

Radiation.	Plane.	Intensity.	Observed. d/n .	Calculated. d/n .
*K α	100 ⁽²⁾	St.	3.263	3.264
K α	10 $\bar{1}$ 0	M.	3.018	3.016
K α	0001 ⁽²⁾	M.	2.887	2.891
K α	10 $\bar{1}$ 1	St.	2.677	2.674
*K α	110 ⁽²⁾	M.	2.359	2.357
*K α	221	M.	2.260	2.260
K α	10 $\bar{1}$ 2	M.	2.09	2.086
*K α	22 $\bar{2}$	M.	1.854	1.859
K α	11 $\bar{2}$ 0 ⁽²⁾	M.	1.742	1.742
K α	10 $\bar{1}$ 3	St.	1.622	{ 1.624
*K α	100 ⁽⁴⁾			{ 1.632
*K α	210 ⁽²⁾	St.	1.493	{ 1.484
K α	11 $\bar{2}$ 2			{ 1.493
K α	20 $\bar{2}$ 1	V.W.	1.463	1.459
*K α	332	M.	1.439	1.449
*K α	431	M.	1.322	1.320
K α	10 $\bar{1}$ 4	W.	1.303	1.303
K α	20 $\bar{2}$ 3	W.	1.186	1.188
K α	12 $\bar{3}$ 1	W.	1.116	1.119
K α	11 $\bar{2}$ 4	W.	1.106	1.112
*K α	100 ⁽⁶⁾	V.W.	1.083	1.088

Mixture of hexagonal close-packed lattice, dimensions $a_0=3.483$ Å.U., $c=1.66$, and a face-centred, rhombohedral lattice, dimensions $a_0=6.540$ Å.U., $\alpha=87^\circ 34'$.

NOTE.—The lines of the face-centred rhombohedral lattice are denoted by *.

are of practically the same size, the small difference in their atomic diameters would not be sufficient to enable a solid solution of the order indicated by Herold to be detected by X-ray analysis.

Table VII. gives the spacings obtained from the powder photograph of the pure metal bismuth. The spacings are those of a face-centred rhombohedral structure, with $a_0 = 6.540$ Å.U. and angle of rhomb $87^\circ 34'$. These agree with the dimensions found by L. W. McKeehan⁽¹⁰⁾, who gave $a_0 = 6.546$ Å.U., angle of rhomb $87^\circ 34'$, but do not agree with those of Ehret and Fine⁽⁴⁾, who found $a_0 = 6.577$ Å.U. and angle $87^\circ 34'$.

TABLE VII.

Bismuth.

Radiation.	Plane.	Intensity.	Observed. d/n .	Calculated. d/n .
K_α	100 ⁽²⁾	St.	3.247	3.264
K_β	110 ⁽²⁾	W.	2.371	2.357
K_α	110 ⁽²⁾	M.	2.353	2.357
K_α	221	M.	2.257	2.260
K_α	311	W.	2.018	2.022
K_α	111 ⁽²⁾	M.	1.965	1.966
K_α	22 $\bar{2}$	M.	1.862	1.859
K_α	100 ⁽⁴⁾	M.	1.630	1.632
K_α	331	W.	1.549	1.549
K_α	210 ⁽²⁾	M.	1.485	1.484
K_α	332	M.	1.438	1.449
K_α	211 ⁽²⁾	W.	1.383	1.381
K_α	431	M.	1.323	1.320
K_α	111 ⁽³⁾	M.	1.307	1.310
K_α	511	W.	1.281	1.278
K_α	432	V.W.	1.256	1.259
K_α	221 ⁽²⁾	V.W.	1.131	1.130
K_α	100 ⁽⁶⁾	V.W.	1.088	1.088
K_α	42 $\bar{4}$	W.	1.069	1.069

Structure: Face-centred rhombohedral.

Dimensions of unit cell $\begin{cases} a_0 = 6.540 \text{ Å.U.} \\ \alpha = 87^\circ 34'. \end{cases}$

α = angle of rhomb.

Discussion of Results for the Lead-Bismuth System.

The crystal structures in the lead-bismuth alloys have been investigated and a new phase existing alone from about 25 to 33 per cent. bismuth has been discovered. If we take into account this phase, then proceeding along the equilibrium diagram from the lead end, addition of

bismuth up to 20 per cent. causes an expansion of the lead lattice from $a_0 = 4.930 \text{ \AA.U.}$ to $a_0 = 4.946 \text{ \AA.U.}$ At this percentage of bismuth the new crystalline phase—an hexagonal close-packed structure—begins to appear. As the percentage of bismuth increases from 20 to 25, the structure gradually transforms from face-centred cubic to hexagonal close-packing until at 25 per cent. bismuth the whole structure is hexagonal. It is interesting to note that at the composition 25 per cent. bismuth one atom in every four is bismuth. Since there are four atoms associated with the face-centred cubic unit cell, it seems that when the proportion of bismuth present is such that one lead atom in every lead cell would be replaced by a bismuth atom, the face-centred cubic structure is not produced on the solidification of the liquid alloy, but the whole alloy sets into the next simplest close-packed arrangement—hexagonal. Returning to the equilibrium diagram, further addition of bismuth to the 25 per cent. bismuth alloy causes a slight expansion of the hexagonal cell $a_0 = 3.477 \text{ \AA.U.}$ until a limit is reached at the 33 per cent. bismuth alloy when $a_0 = 3.483 \text{ \AA.U.}$, the axial ratio remaining constant at $c = 1.66$. From 33 per cent. bismuth to 100 per cent. bismuth the crystal structures of the alloys consist of the hexagonal close-packed lattice $a_0 = 3.483 \text{ \AA.U.}$, $c = 1.66$, and the face-centred rhombohedral lattice of bismuth.

The atomic diameter of bismuth is only slightly larger than that of lead, and it has therefore not been possible to fix for certain the limits of the solid solution and those of the hexagonal phase. All evidence points to the conclusion that the solid solution of bismuth in lead (face-centred cubic) extends to just under 20 per cent. bismuth, while there is a further solution up to 33 per cent. bismuth where the structure is hexagonal close-packed. It is impossible to detect by X-ray analysis the solid solution of lead in bismuth owing to the small solution—1 per cent.—and to the atoms of lead and bismuth being practically the same size.

It would appear that the formation of the hexagonal phase following the solution of bismuth in the face-centred cubic lattice of lead is similar to the formation of the hexagonal phase in the copper-antimony⁽¹⁾ system, which also follows the limit of the solution of antimony in the face-centred cubic lattice of copper.

Several films were taken of the pure metal bismuth, the measurement of the lattice constant $a_0 = 6.540 \text{ \AA.U.}$ agreeing to within one-tenth of 1 per cent. with that found by L. W. McKeehan⁽¹⁰⁾ — $a_0 = 6.546 \text{ \AA.U.}$, but there is a difference of $.037 \text{ \AA.U.}$ between the value found and that given by Ehret and Fine⁽⁴⁾.

The difference between the experimentally determined values of the specific heats of the lead-bismuth alloys by O. Richter⁽⁶⁾ and those calculated from the rule of mixtures is doubtless explained by the solid solution present

TABLE VIII.

Tin.

Plane.	Intensity.	Observed. $d/n.$	Calculated. $d/n.$
100 ^(*)	St.	2.909	2.909
101	St.	2.785	2.786
120	W.	2.600	2.602
111	W.	2.516	2.513
110 ⁽²⁾	M.	2.051	2.057
121	St.	2.011	2.012
301	M.	2.658	1.655
112	M.	1.489	1.481
231	M.	1.442	1.438
120 ^(*)	W.	1.303	1.301
141	W.	1.291	1.290
132	M.	1.201	1.202
541	M.	1.092	1.092

Structure : Simple tetragonal.

Dimensions of unit cell $\begin{cases} a_0 = 5.818 \text{ \AA.U.} \\ a_3 = 3.174 \text{ \AA.U.} \\ c = .546. \end{cases}$

up to 20 per cent. bismuth and to the presence, in the alloys containing more than 20 per cent. bismuth, of the hexagonal close-packed structure—a structure different from that of either of the component elements.

The Tin-Bismuth System.

X-radiograms of tetragonal tin have been examined, and earlier workers gave the dimensions of the tetragonal lattice as $a_0 = 5.84 \text{ \AA.U.}$, $c = .406$. The spacings obtained from a powder photograph of pure tin are given in Table IX., and the dimensions of the lattice deduced from these results are $a_0 = 5.818 \text{ \AA.U.}$, $a_3 = 3.174 \text{ \AA.U.}$, giving an

axial ratio of $c=546$. Westgren and Phragmén⁽¹¹⁾, working on the copper-tin system, also found the same values.

A film of an annealed specimen of the alloy 50 per cent. tin, 50 per cent. bismuth was taken, and the spacings deduced from measurements on the film are given in Table IX.

TABLE IX.

Alloy of composition :—50 per cent. bismuth ; 50 per cent. tin.

Plane.	Intensity.	Observed. d/n .	Calculated. d/n .
100 ⁽²⁾	St.	3.263	3.264
*100 ⁽²⁾	St.	2.908	2.909
*101	St.	2.788	2.786
110 ⁽²⁾	M.	2.361	2.357
221	M.	2.264	2.260
*110 ⁽²⁾	M.	2.055	2.057
*121	St.	2.014	2.012
111 ⁽²⁾	M.	1.971	1.966
22 $\bar{2}$	M.	1.860	1.859
*301	M.	1.655	1.655
100 ⁽⁴⁾	M.	1.631	1.632
*112	M.	1.480	1.481
*231	M.	1.435	1.438
431	M.	1.321	1.320
*120 ⁽²⁾	W.	1.300	1.301
511	W.	1.285	1.278
432	V.W.	1.253	1.259
*132	M.	1.198	1.202
221 ⁽²⁾	V.W.	1.130	1.130
100 ⁽⁶⁾	V.W.	1.088	1.088
424	W.	1.067	1.069

Structure : Mixture of

(1) The face-centred rhombohedral lattice of bismuth, dimensions $a_0=6.540$ A.U. and $\alpha=87^\circ 34'$.

(2) The tetragonal lattice of tin, dimensions $a_0=5.818$ Å.U., $a_3=3.174$ A.U. and $c=546$.

The planes of the tetragonal lattice of tin are denoted by *

These spacings were compared with the spacings of pure tin and pure bismuth, and every line on the photograph was accounted for as belonging to either the tetragonal tin lattice or the rhombohedral bismuth lattice. As the lattices in the alloy 50 per cent. tin, 50 per cent. bismuth are those of tin and bismuth, the crystal structures of all alloys of tin and bismuth are mixtures of the lattices of these two metals in unaltered dimensions.

James and Evans⁽¹²⁾, working on the galvano-magnetic effects of the tin-bismuth alloys have obtained results which indicate no solubility of bismuth in tin and a small solubility of .5 per cent. by weight of tin in bismuth. As no change in the size of the lattices of bismuth and tin is observed in the present investigation, the region of solid solution at the bismuth end of the equilibrium indicated by the results of James and Evans is probably not more than that stated, which is not sufficient to produce a measurable change in the size of the bismuth lattice.

The crystal structures of the lead-bismuth and tin-bismuth systems are different from those of the lead-antimony⁽²⁾ and tin-antimony⁽³⁾ systems, although the crystal structures of antimony and bismuth are alike. Whereas lead easily takes bismuth into solid solution, antimony is practically insoluble in lead. Lead, however, is practically insoluble in bismuth and antimony. From work on the tin-antimony system, tin and antimony form a compound SnSb having a sodium-chloride structure, and regions of solid solution exist both at the tin end and the antimony end of the equilibrium diagram. Alloys of tin and bismuth, on the other hand, are just mixtures of the crystalline phases of the component elements. Again, copper-bismuth⁽⁴⁾ alloys are mechanical mixtures of the two metals, while copper and antimony when alloyed together form a compound Cu_2Sb and also solid solutions.

In conclusion we wish to thank Professor E. J. Evans for facilities for carrying out this investigation and for his continued interest during its progress.

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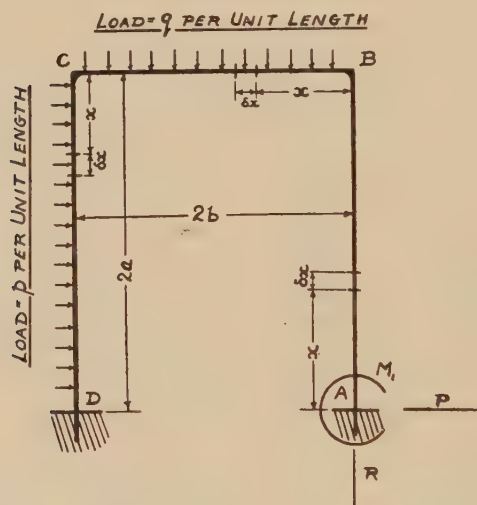
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XCII. *General Solution of the Portal Frame Structure for the Determination of the Fixing Couples and Reactions at the Joints.* By C. E. LARARD, M.Inst.C.E.*

CONSIDER the portal frame structure represented in fig. 1.

AB and CD are two vertical members or columns fixed at the bases and of uniform sections having second moments of area of cross-sections represented by I and nI respectively, and BC is a horizontal cross member or beam of uniform section

Fig. 1.



whose second moment of area is mI and whose ends B and C are fixed jointed to the tops of the columns. The vertical member CD supports p units of load per unit length and BC a horizontal load of q units per unit length.

The determination of the magnitudes and directions of the moment couples and reactions at A, B, C, and D can be evaluated when the two forces P and R and the couple M_1 at the foot of one of the columns are determined (see fig. 1).

The author gives the following general solution of this problem, using the principle of minimum internal or strain-energy, taking into account the work of flexure for each of the three members.

* Communicated by the Author.

Let the work done in bending AB, BC, and CD, and therefore stored up in these members, be denoted by U_{AB} , U_{BC} , and U_{CD} respectively, and let the total work

$$U = U_{AB} + U_{BC} + U_{CD}. \quad (1)$$

Since the forces P and R produce no displacements of A in their line of action, then

$$\frac{\partial U}{\partial P} = 0, \quad \frac{\partial U}{\partial R} = 0,$$

and also since the couple M_1 produces no angular rotation

$$\frac{\partial U}{\partial M_1} = 0.$$

$$\therefore \frac{\partial U}{\partial M_1} = \frac{\partial U_{AB}}{\partial M_1} + \frac{\partial U_{BC}}{\partial M_1} + \frac{\partial U_{CD}}{\partial M_1} = 0, \quad (2)$$

$$\frac{\partial U}{\partial P} = \frac{\partial U_{AB}}{\partial P} + \frac{\partial U_{BC}}{\partial P} + \frac{\partial U_{CD}}{\partial P} = 0, \quad (3)$$

$$\frac{\partial U}{\partial R} = \frac{\partial U_{AB}}{\partial R} + \frac{\partial U_{BC}}{\partial R} + \frac{\partial U_{CD}}{\partial R} = 0. \quad (4)$$

Now the work of flexure for an element of length δx of an elastic material is given by $\frac{M^2 \delta x}{2EI_0}$, where M is the variable bending moment, E Young's modulus of elasticity, and I_0 the second moment of area of the cross-section of the element with respect to the trace of the neutral surface on the plane of the cross-section.

The work function for the structure then becomes

$$U = \Sigma \int_0^L \frac{M^2}{2EI_0} \cdot dx,$$

where L stands for the length of each flexed member in turn.

For the structure under consideration and referring to fig. 1 we have therefore from equation (1)

$$U = \frac{1}{2EI_0} \int_0^{2a} M^2 \cdot dx + \frac{1}{mEI_0} \int_0^{2b} M^2 \cdot dx + \frac{1}{nEI_0} \int_0^{2a} M^2 \cdot dx. \quad (5)$$

Differentiating equation (5) in turn with respect to M_1 , P, and R, and equating to zero as indicated in equations (2), (3), and (4), we obtain

$$\frac{\partial U}{\partial M_1} = \int_0^{2a} M \frac{\partial M}{\partial M_1} dx + \frac{1}{m} \int_0^{2b} M \frac{\partial M}{\partial M_1} dx + \frac{1}{n} \int_0^{2a} M \frac{\partial M}{\partial M_1} dx = 0, \quad (6)$$

$$\frac{\partial U}{\partial P} = \int_0^{2a} M \frac{\partial M}{\partial P} dx + \frac{1}{n} \int_0^{2b} M \frac{\partial M}{\partial P} dx + \frac{1}{n} \int_0^{2a} M \frac{\partial M}{\partial P} = 0, \quad \dots \quad (7)$$

$$\frac{\partial U}{\partial R} = \int_0^{2a} M \frac{\partial M}{\partial R} dx + \frac{1}{n} \int_0^{2b} M \frac{\partial M}{\partial R} dx + \frac{1}{n} \int_0^{2a} M \frac{\partial M}{\partial R} = 0. \quad \dots \quad (8)$$

For the member AB :

$$M = M_1 + Px, \quad \dots \quad (9)$$

and

$$\frac{\partial M}{\partial M_1} = 1, \quad \frac{\partial M}{\partial P} = x, \quad \frac{\partial M}{\partial R} = 0.$$

For the member BC :

$$M = M_1 + 2aP + Rx - \frac{1}{2}qx^2, \quad \dots \quad (10)$$

and

$$\frac{\partial M}{\partial M_1} = 1, \quad \frac{\partial M}{\partial P} = 2a, \quad \frac{\partial M}{\partial R} = x.$$

For the member CD :

$$M = M_1 + P(2a - x) + 2bR - 2b^2q - \frac{1}{2}px^2, \quad \dots \quad (11)$$

and

$$\frac{\partial M}{\partial M_1} = 1, \quad \frac{\partial M}{\partial P} = (2a - x), \quad \frac{\partial M}{\partial R} = 2b.$$

Substituting in turn the values of M given in equations (9), (10), and (11) and their differentials in equations (6), (7), and (8):

Equation (6) becomes

$$\begin{aligned} \frac{\partial U}{\partial M_1} = & \int_0^{2a} (M_1 + Px) dx + \frac{1}{n} \int_0^{2b} (M_1 + 2aP + Rx - \frac{1}{2}qx^2) dx \\ & + \frac{1}{n} \int_0^{2a} \{M_1 + (2a - x)P + 2bR - 2b^2q - \frac{1}{2}px^2\} dx = 0, \quad (12) \end{aligned}$$

which on integration and simplification takes the form

$$\begin{aligned} (amn + 1 + bn)M_1 + a(amn + 1 + 2bn)P + b(2am + bn)R \\ - \frac{2}{3}a^3mp - 2b^2(am + \frac{1}{3}bn)q = 0. \quad \dots \quad (13) \end{aligned}$$

Equation (7) becomes

$$\begin{aligned} \frac{\partial U}{\partial P} = & \int_0^{2a} (M_1 + Px)x dx + \frac{1}{n} \int_0^{2b} (M_1 + 2aP + Rx - \frac{1}{2}qx^2)2a \cdot dx \\ & + \frac{1}{n} \int_0^{2a} \{M_1 + P(2a - x) + 2bR - 2b^2q - \frac{1}{2}px^2\}(2a - x) dx = 0. \quad \dots \quad (14) \end{aligned}$$

Reducing to

$$(amn + 1 + 2bn)M_1 + 4a(\frac{1}{3}amn + 1 + bn)P + 2b(am + bn)R - \frac{1}{3}a^3mp - 2b^2(am + \frac{2}{3}bn)q = 0, \quad . \quad . \quad . \quad (15)$$

Equation (8) becomes

$$\begin{aligned} \frac{\partial U}{\partial R} &= \frac{1}{m} \int_0^{2b} M_1 + 2aP + Rx - \frac{1}{2}qx^2) x \, dx \\ &+ \frac{1}{n} \int_0^{2a} \{M_1 + P(2a - x) + 2bR - 2b^2q - \frac{1}{2}px^2\} 2b \, dx = 0, \end{aligned} \quad . \quad . \quad . \quad (16)$$

simplifying to

$$(2am + bn)M_1 + 2a(am + bn)P + 4b(am + \frac{1}{3}bn)R - \frac{4}{3}a^3mp - b^2(4am + bn)q = 0. \quad . \quad . \quad . \quad (17)$$

The solution of the simultaneous equations (13), (15) and (17) gives the values

$$\begin{aligned} M_1 &= \frac{1}{2V} \left[a^2 \left(2a^2m^2 + \frac{22n+13}{9}abm + b^2n \right) p \right. \\ &\quad \left. + b^3 \left(\frac{5n-1}{3}am + \frac{n+1}{9}bn \right) q \right], \end{aligned} \quad (18)$$

$$\begin{aligned} P &= -\frac{1}{4aV} \left[a^2(4a^2m^2 + \frac{4}{3}4n + 1abm + b^2n)p \right. \\ &\quad \left. + b^3n(4am + \frac{1}{3}n + 1b) \right], \quad . \quad . \quad (19) \end{aligned}$$

$$\begin{aligned} R &= \frac{1}{4bV} \left[a^3m(\frac{4}{3}amn + 1 + \frac{1}{3}17n - 1b)p \right. \\ &\quad \left. + 2b^2 \left\{ 2(n+1)a^2m^2 + \left(\frac{n^2}{2} + \frac{22n}{3} + \frac{5}{6} \right) abm + \frac{2}{3}(n+1)b^2n \right\} q \right], \end{aligned} \quad . \quad . \quad . \quad (20)$$

where for each of the above equations V has the value

$$V = (n+1)(a^2m^2 + \frac{1}{3}abmn + 1 + \frac{1}{3}b^2n) + 3abmn. \quad (21)$$

The fixing couple M_1 at the foot of the column AB being positive acts in the counter-clockwise direction.

The sign of P being negative indicates that P gives a clockwise moment at any point in the structure, and R being positive indicates a counter-clockwise moment about any point.

Fig. 2 shows the action of the forces and reactions at A, B, C, and D.

For any permissible values of a , b , m , n , p , and q the magnitudes of M_1 , P , and R are arrived at by substitution in equations (18) to (21).

The moments at B, C, and D can then be found by taking simple moments at these points ; thus

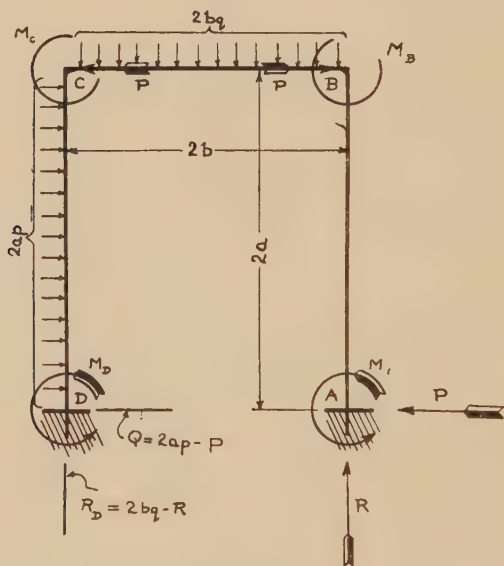
$$M_B = M_1 + 2aP, \quad \dots \dots \dots (22)$$

$$M_C = M_1 + 2aP + 2bR - 2b^2q, \quad \dots \dots (23)$$

$$M_D = M_1 + 2bR - 2b^2q - 2a^2p. \quad \dots \dots (24)$$

The horizontal reaction, Q, at D is found from the condition that the sum of P and Q is equal in magnitude but

Fig. 2.



opposite in direction to the force $2ap$, whilst the vertical reaction R at D is found from

$$R + R_D = 2aq.$$

The above investigation gives the most general and at the same time the most tedious problem to solve on the portal frame, but particular cases can be derived quite simply from the results given; and several of these are of sufficient importance to receive attention.

Special Cases.

1. The two columns AB and CD with the same value of the second moment of area, *i.e.*, $n = 1$.

In this case writing $n = 1$ in equations (18) to (21) we obtain

$$M_1 = \frac{a^2(18a^2m + 35abm + 9b^2)p + 2b^3(6am + b)q}{6(6am + b)(am + 2b)}, \quad (25)$$

$$P = -\frac{a^2(2am + 3b)p + 2b^3q}{4a(am + 2b)}, \quad (26)$$

$$R = \frac{2a^3mp + b^2(6am + b)q}{b(6am + b)}. \quad (27)$$

2. If all three members are of like cross-section then m should be written equal to unity in the last three equations.

3. *Frame pin jointed at A with fixed joints at BCD.*

Write $M_1 = 0$ in equations (15) and (17), which then become

$$4a(amn + 1 + 3bn)P + 6b(am + bn)R - a^3mp - 2b^2(3am + 2bn)q = 0, \quad (28)$$

$$6a(am + bn)P + 4b(3am + bn)R - 4a^3mp - 3b^2(4am + bn)q = 0. \quad (29)$$

The unknown reactions P and R can then be determined by solving the simultaneous equations (28) and (29). . . (30)

4. *Frame pin jointed at D only.*

Moments at D gives

$$M_1 + 2bR - 2a^2p - 2b^2q = 0, \quad (31)$$

from which

$$R = \frac{2a^2p + 2b^2q - M_1}{2b}. \quad (32)$$

For the member AB:

$$M = M_1 + Px, \quad \frac{\partial M}{\partial M_1} = 1, \quad \frac{\partial M}{\partial P} = x,$$

$$\frac{\partial U_{AB}}{\partial M_1} = \frac{1}{EI} \int_0^{2a} (M_1 + Px) dx = \frac{1}{EI} (2aM_1 + 2a^2P), \quad (33)$$

$$\frac{\partial U_{AB}}{\partial P} = \frac{1}{EI} \int_0^{2a} (M_1 + Px) x dx = \frac{1}{EI} (2a^2M_1 + \frac{8}{3}a^3P). \quad (34)$$

Member BC:

$$\begin{aligned} M &= M_1 + 2aP + Rx - \frac{1}{2}qx^2 \\ &= M_1 + 2aP + \frac{2a^2p + 2b^2q - M_1}{2b} \cdot x - \frac{1}{2}qx^2 \end{aligned}$$

$$= M_1 \left(1 - \frac{x}{2b} \right) + 2aP + \frac{a^2 p}{b} x + \left(bx - \frac{x^2}{2} \right) q, \quad (35)$$

$$\frac{\partial M}{\partial M_1} = \left(1 - \frac{x}{2b} \right), \quad \frac{\partial M}{\partial P} = 2a,$$

$$\frac{\partial U_{BC}}{\partial M_1} = \frac{1}{Em} \int_0^{2b} \left\{ M_1 \left(1 - \frac{x}{2b} \right) + 2aP + \frac{a^2 p}{b} x + \left(bx - \frac{x^2}{2} \right) q \right\} \left(1 - \frac{x}{2b} \right) dx \quad (36)$$

$$= \frac{1}{EmI} \left(\frac{2}{3} b M_1 + 2abP + \frac{2}{3} a^2 bp + \frac{1}{3} b^3 q \right), \quad (37)$$

$$\frac{\partial U_{BC}}{\partial P} = \frac{1}{EmI} \int_0^{2b} \left\{ M_1 \left(1 - \frac{x}{2b} \right) + 2aP + \frac{a^2 p}{b} x + \left(bx - \frac{x^2}{2} \right) q \right\} 2a \cdot dx \quad (38)$$

$$= \frac{1}{EmI} (2abM_1 + 8a^2bP + 4a^3bp + \frac{4}{3}ab^3q). \quad (39)$$

Member CD :

$$\begin{aligned} \bar{M} &= M_1 + P(2a-x) + 2bR - 2b^2q - \frac{1}{2}px^2 \\ &= P(2a-x) + p \left(2a^2 - \frac{x^2}{2} \right), \end{aligned} \quad (40)$$

$$\frac{\partial \bar{M}}{\partial M_1} = 0, \quad \frac{\partial \bar{M}}{\partial P} = (2a-x),$$

$$\frac{\partial U_{CD}}{\partial P} = \frac{1}{EnI} \int_0^{2a} \left\{ P(2a-x) + p \left(2a^2 - \frac{x^2}{2} \right) \right\} (2a-x) dx \quad (41)$$

$$= \frac{1}{EnI} \left(\frac{8}{3} a^3 P + \frac{10}{3} a^4 p \right). \quad (42)$$

Equation (6) then becomes

$$\frac{\partial U}{\partial M_1} = (33) + (37)$$

$$= (2aM_1 + 2a^2P) + \frac{1}{m} \left(\frac{2}{3} b M_1 + 2abP + \frac{2}{3} a^2 bp + \frac{1}{3} b^3 q \right) = 0, \quad (43)$$

reducing to

$$2M_1(3am+b) + 6aP(am+b) + 2a^2bp + b^3q = 0. \quad (44)$$

Equation (7) takes the form (34) + (39) + (42) = 0.

$$\frac{\partial U}{\partial P} = (2a^2M_1 + \frac{8}{3}a^3P) + \frac{1}{m} (2abM_1 + 8a^2bP + 4a^3bp + \frac{4}{3}ab^3q) + \frac{1}{n} \left(\frac{8}{3}a^3P + \frac{10}{3}a^4p \right) = 0, \quad \dots \quad (45)$$

reducing to

$$3nM_1(am + b) + 4aP(amn + 1 + 3bn) + a^2p(5am + 6bn) + 2b^3nq = 0. \quad \dots \quad (46)$$

The solution of the simultaneous equations (44) and (46) gives the values of M_1 and P .

5. *Frame pin jointed at A and D.*

For the member AB :

$$M = Px, \quad \frac{\partial M}{\partial P} = x;$$

for BC :

$$M = 2aP + Rx - \frac{1}{2}qx^2, \quad \frac{\partial M}{\partial P} = 2a;$$

for CD :

$$M = P(2a - x) + 2bR - 2b^2q - \frac{1}{2}px^2, \quad \frac{\partial M}{\partial P} = (2a - x).$$

Simple moments at D gives

$$R = \frac{b^2q + a^2p}{b}. \quad \dots \quad (47)$$

For the three members AB, BC, and CD, total work = U .

$$\begin{aligned} \frac{\partial U}{\partial P} = & \int_0^{2a} (Px)x dx + \frac{1}{m} \int_0^{2b} (2aP + Rx - \frac{1}{2}qx^2)2a \cdot dx \\ & + \frac{1}{n} \int_0^{2a} \{P(2a - x) + 2bR - 2b^2q - \frac{1}{2}px^2\}(2a - x)dx = 0. \end{aligned} \quad \dots \quad (48)$$

Equation (48) reduces to

$$4a(\frac{1}{3}amn + 1 + bn)P + 2bR(am + bn) - 2b^2(\frac{2}{3}bn + am)q - \frac{1}{3}a^3mp = 0. \quad \dots \quad (49)$$

In this equation substitute (47) for R . Solving for P , we have

$$P = - \frac{a^2(5am + 6bn)p + 2b^3nq}{4a(amn + 1 + 3bn)}. \quad \dots \quad (50)$$

6. *If AB and CD have like cross-sections $n=1$, and from (50) above*

$$P = - \frac{a^2(5am + 6bn)p + 2b^3q}{4a(2am + 3b)}. \quad \dots \quad (51)$$

7. *Frame pin jointed at B and C.*

In this case $R = qb$.

Member AB :

$$M = Px, \quad \frac{\partial U}{\partial P} x,$$

where x = distance from B along AB and where P = the reaction along CB = $-P$ at A.

Member BC :

$$M = bqx - \frac{1}{2}qx^2, \quad \frac{\partial M}{\partial P} = 0.$$

Member CD :

$$M = Px - \frac{1}{2}px^2, \quad \frac{\partial M}{\partial P} = x.$$

The differential of the total work function U then becomes

$$\frac{\partial U}{\partial P} = \int_0^{2a} (Px)x \cdot dx + \frac{1}{n} \int_0^{2a} (Px - \frac{1}{2}px^2)x dx = 0, \quad \dots \quad (52)$$

which on solution gives the value

$$P = \frac{3ap}{4(n+1)}, \quad \dots \dots \dots (53)$$

Then

$$M_1 = -(-Px2a) \\ = 2a \frac{3ap}{4(n+1)} = \frac{3a^2p}{2(n+1)}, \quad \dots \dots \dots (54)$$

$$Q = 2ap - P = \frac{8n+5}{4(n+1)}ap, \quad \dots \dots \dots (55)$$

$$M_2 = 2aP - 2a^2p = \frac{4n+1}{2(n+1)}a^2p. \quad \dots \dots (56)$$

XCI. *Uniform Columns in Electric Discharges.* By J. S. TOWNSEND, M.A., F.R.S., Wykeham Professor of Physics, Oxford*.

1. **T**HE theory † which I gave some years ago to account for the conductivity in the uniform positive column of a discharge through a rarefied gas has been found to give a satisfactory explanation of the experiments that have been made at the Electrical Laboratory, Oxford, on the uniform

* Communicated by the Author.

† 'Electricity in Gases,' Section 302.

luminous columns obtained either in direct current or in oscillatory current discharges.

The forces required to maintain the discharges are comparatively small, and in many cases the mean energy of agitation E_1 of the electrons is about three or four volts ; so that the mean loss of energy of an electron in a collision with a molecule of the gas is a small fraction of the mean energy E_1 .

The principal phenomena observed in luminous discharges are due to collisions in which the energies of the electrons are greater than the mean energy E_1 . In some of these collisions the molecules of the gas are ionized, and in others the amount of energy transferred to the molecules is sufficient to excite radiation.

The experiments show that the mean energy of the electrons which excite the red lines of the spectrum is less than the mean energy of those which excite yellow lines, and this energy is less than the mean energy of the electrons that excite green or violet lines. An example of the method of finding the energies of the electrons that excite the lines in different parts of the spectrum is given in the paper on the excitation of the helium spectrum*.

A similar method may be used to find the energies of the electrons in the collisions in which the molecules are ionized in luminous discharges.

The coefficients of ionization α corresponding to the electric forces Z and gas pressure p in these discharges are very small, and it is necessary to find the values of α from the general theory of the discharges, as these values of α/p have not been determined by the ordinary method in terms of the ratio Z/p .

In the account of the theory which I gave † to explain the luminous columns in high-frequency discharges it was shown that there is a simple relation between the coefficient of ionization and the coefficients of diffusion and the mobilities of the positive ions and the electrons.

It is convenient to give here the method of determining this relation between the coefficients, and to limit the investigation to the conductivity obtained in direct current discharges. The experiments show that the mean electric force in the uniform columns of high-frequency discharges is the same as the force in the uniform positive column of a direct current discharge, so that the same formula connecting the coefficients applies to both types of discharge.

* J. S. Townsend and F. Llewellyn Jones, *Phil. Mag.* xi. p. 679 (March 1931).

† *Comptes Rendus*, clxxxvi. p. 55 (9th Jan. 1928).

It has been found that for a given pressure of the gas the electric force Z parallel to the axis of the tube in the uniform column of a discharge is within wide limits independent of the intensity of the current through the gas. This result has been obtained with small currents in tubes of different diameters, from about 1 centimetre to 4 centimetres, containing gases at different pressures. With large currents exceeding 10 milliamperes the force diminishes, due to the rise in temperature of the gas. The theory of the discharge depends principally on the experiments with the smaller currents, where the force is independent of the intensity of the current.

2. In a long uniform column the force Z is the same at all distances z from a fixed plane perpendicular to the axis of the tube, so that the velocities and coefficients of diffusion of the electrons and positive ions are independent of the ordinate z . Let n be the number of electrons per cubic centimetre at a point in the gas at a distance r from the axis of the tube, q the number in a cylinder of unit length coaxial with the tube and of radius r . This number is given

by the integral $\int_0^r 2\pi n r dr$, and if a be the radius of the tube

the integral, from $r=0$ to $r=a$, represents the number of electrons Q between two planes perpendicular to the axis of the tube at 1 centimetre apart. Let n' , q' , and Q' be the corresponding numbers for the positive ions. The current in the tube is given by the expression $e(Qw + Q'w')Z$, where wZ and $w'Z$ are the velocities, in the direction of the axis, of the electrons and positive ions respectively. The quantity $e(Q' - Q)$ must be small compared with eQ or eQ' , in order that the charge in the gas may not give rise to a force larger than the force Z . The velocities have been determined in terms of the ratio Z/p , and since w is much greater than w' the second term may be neglected in the above expression for the current, and the number Q is then found from the current flowing in the tube.

There is a positive charge in the gas and a corresponding force R along the radius. The value of R at the distance r from the axis is $2e(q' - q)/r$. It is small compared with the force Z , and in general the quantity $(q' - q)$ may be taken to be less than $q/100$.

Since the force Z is the same for all currents, the velocities wZ and $w'Z$ are independent of the current and the numbers Q and Q' are proportional to the current.

3. When the current is steady, the rate of increase of these quantities due to ionization by collision is balanced by the rate at which the electrons and positive ions disappear from the gas by flowing to the surface of the tube. In unit volume of the gas the rate at which n and n' increase due to ionization by collision is given by the equations

$$dn/dt = dn'/dt = \alpha n w Z,$$

where α is the coefficient of ionization. This rate of increase is proportional to n , so that the rate at which the electrons and positive ions disappear is also proportional to n . It follows therefore that the disappearance cannot be attributed to recombination in the gas, since the rate of loss by this process is proportional to n^2 . Thus the effect of recombination in the gas may be neglected in considering a theory of the conductivity of luminous columns in discharges.

The electrons diffuse to the sides more rapidly than the positive ions, and a positive charge accumulates in the gas due to an excess of positive ions over electrons. The force along the radius due to the positive charge retards the flow of electrons towards the surface of the tube and increases the flow of the positive ions. A steady state is reached when both positive ions and electrons flow towards the sides at the same rate as that at which they are generated by the process of ionization by collision. This condition is expressed by the following equations, where the term on the left represents the rate at which electrons and positive ions are generated in a cylinder of unit length and radius r , and the terms on the right represent the flow through the surface of the cylinder. In equation (1) K is the coefficient of diffusion of the electrons, and the first term on the right represents the flow of the electrons due to diffusion, which is diminished by the action of the force R , as shown by the second term on the right. In equation (2) K' is the coefficient of diffusion of the positive ions, and in this case the effect of diffusion is increased by the electric force R .

$$\alpha q w Z = -2\pi r K dn/dr - 2\pi r n w R, \quad . \quad . \quad (1)$$

$$\alpha q w Z = -2\pi r K' dn'/dr + 2\pi r n' w' R. \quad . \quad . \quad (2)$$

4. From these equations the following equation is obtained for n in terms of r , ($n - n'$) being neglected in comparison with n :

$$2\pi(Kw' + K'w)r dn/dr + \alpha q w(w + w')Z = 0. \quad . \quad (3)$$

It is seen, by comparing equations, (1) and (3), that the effect of the force R on the motion of the electrons is

the same as if the coefficient of diffusion K were reduced to $(Kw' + K'w)/(w + w')$, which is approximately equal to Kw'/w .

The differential equation for n obtained from equation (3) is

$$(Kw' + K'w) \left(\frac{d^2 n}{dr^2} + \frac{1}{r} \frac{dn}{dr} \right) + \alpha w(w + w') Zn = 0, \quad (4)$$

and the solution is

$$n = AJ_0(cr), \quad (5)$$

$$\text{where} \quad c^2 = \frac{\alpha w(w + w') Z}{Kw' + K'w}. \quad (6)$$

This equation for c^2 may be simplified by taking into consideration the values of the ratios w/K and w'/K' . It has been found from the investigations of the motions of ions and electrons in gases that the ratio w'/K' is 1.23×10^4 , the atomic charge e and the electric forces being expressed in electrostatic units. The ratio w/K is $1.23 \times 10^4/k$, where k is the factor by which the mean energy of agitation of the electrons exceeds the mean energy of agitation of molecules of a gas at 15°C . In the uniform luminous discharges k is of the order 100, so that Kw' is large compared with $K'w$. Also w is large compared with w' . Neglecting quantities of a small order of magnitude, equation (6) becomes approximately

$$c^2 = \frac{\alpha w}{w'} \times \frac{41 \times Z}{k}, \quad (7)$$

the force Z being expressed in volts per centimetre.

The value of c could be found from equation (5) if the ratio of the values of n at two different distances r from the axis were known. In that equation A is the value of n at the axis ($r=0$), and if yA be the value of n near the surface of the tube ($r=a$), the value of c would be given by the equation $J_0(ca) = y$. The variation of n along the radius has not been measured accurately, but in order to form an approximate estimate of the coefficient α the factor y may be taken as $\cdot 5$, so that $(c \times a)$ is the root (1.52) of the equation $J_0(x) = \cdot 5$. Thus, with a tube 3 centimetres in diameter c is 1.0 , and equation (7) becomes

$$\alpha = \frac{w'}{w} \times \frac{k}{41 \times Z}. \quad (8)$$

5. The following equation for R in terms of Z is obtained from equations (1) and (2):

$$2\pi r R(nwK' + n'w'K) = (K - K')\alpha qwZ, \quad (9)$$

and as K' is small compared with K the equation may be written in the form

$$\frac{R}{Z} = \frac{\alpha w q}{2\pi r w' n} = \frac{\alpha w}{w'} \times \frac{1}{c^2 n} \times \frac{dn}{dr} \cdot \cdot \cdot \cdot (10)$$

This equation shows that R is independent of the intensity of the current, since n occurs both in the numerator and the denominator in the expression for R/Z . This expression is simplified by taking the value of dn/ndr as given by the first three terms in the expansion of the Bessel function $J_0(cr)$ and $\alpha w/w'$ as given by equation (8). Equation (10) thus becomes

$$\frac{R}{Z} = \frac{k}{41 \times Z} \times \frac{4r}{(8 - c^2 r^2)} \cdot \cdot \cdot \cdot (11)$$

This may be further simplified in order to obtain an approximate estimate of R/Z by omitting $c^2 r^2$ in the denominator of the last term. Thus, $R/Z = kr/82Z$. As the pressure is increased the force Z increases and k diminishes, so that R diminishes in comparison with Z . Thus in helium, in a tube 3 cm. in diameter, the ratio of the forces R/Z is $r/5$ when the gas is at 3 millimetres pressure, and $r/15.6$ at 10 millimetres pressure. In neon in a tube of the same diameter the ratio R/Z is $r/2.7$ when the pressure is 9 millimetres, and $r/9$ when the pressure is 30 millimetres.

These figures show that at the higher pressures the resultant force $\sqrt{R^2 + Z^2}$ is approximately equal to Z . Since the force R increases in importance as the pressure is reduced, the loss of energy of the electrons as they diffuse towards the surface of the tube becomes appreciable.

The variation in the energy of agitation along the radius is easily seen in neon by the change in colour of the discharge. The intensity of the yellow in comparison with the red rays is greater at points near the axis than at points near the surface.

There is also a small change of force due to the current which becomes appreciable with large currents. The increase of temperature of the gas tends to diminish the force required to maintain the current, so that with large currents the force Z is somewhat less than with small currents.

6. The values of Z for luminous discharges in helium* and in neon† at various pressures in a tube 2.9 centimetres internal diameter are given in Tables I. and II. The values of $\alpha \times 10^3$, given in the fourth column of each table, are

* P. Llewellyn Jones, *Phil. Mag.* xi. p. 163, Jan. 1931.

† P. Johnson, *Phil. Mag.* x. p. 921, Nov. 1930.

obtained by equation (8) from the values of w , w' , and k which were found experimentally.

The velocities wZ and the coefficients k , corresponding to the values of Z/p in the tables, are given in the papers on the motion of electrons in helium* and in neon†.

The mean energy of agitation (E_1) of the electrons expressed in volts is approximately $2Z/p$ in helium and $10.5 \times Z/p$ in neon.

The velocities of the positive ions have been determined by Huxley‡. Expressing the velocity in the form bZ/p , he found that in helium the coefficient b is a constant, 2.27×10^4 , for values of Z/p less than the value 2.5, Z being in volts per centimetre and p in millimetres of mercury. This gave $2.27 \times 10^4/p$ as the value of w' for calculating the

TABLE I.—Helium.

p .	Z .	Z/p .	$\alpha \times 10^3$.
22	34	1.55	1.9
16	26.5	1.66	2.9
12	21	1.77	3.7
9	17	1.89	5.1
6	12.3	2.05	7.7
3	7.3	2.43	15.6

TABLE II.—Neon.

p .	Z .	Z/p .	$\alpha \times 10^3$.
50	19	.38	3.5
40	16.2	.405	4.3
30	12.5	.42	5.9
20	9.0	.45	9.0
15	7.6	.51	12.6
10	5.7	.57	20.0

values of α for helium. In neon the velocities of the positive ions were not determined for values of Z/p as small as those given in Table II. The lowest velocity that was measured was 3.2×10^4 centimetres per second, corresponding to $Z/p = .8$, and in order to find the coefficient α for neon w' was taken to be $4 \times 10^4/p$.

7. In order to account for the conductivity in the uniform luminous columns of the gases at the pressures where the mean energy of agitation E_1 of the electrons is about 3 or

* J. S. Townsend and V. A. Bailey, *Phil. Mag.* xlv. p. 657 (Oct. 1923).

† V. A. Bailey, *Phil. Mag.* xlvii. p. 379 (1924).

‡ L. G. H. Huxley, *Phil. Mag.* v. p. 721 (April 1928).

4 volts, it is necessary to form a theory of ionization which is consistent with the values of α given in the above tables.

It may be assumed that the mean energy E_x of the electrons in the collisions with atoms that are ionized is much greater than the mean energy E_1 of all the electrons.

The number of atoms that are ionized is very small compared with the number of collisions in which the energies of the electrons exceed the energy E_x , so that the probability of ionization in a collision is very small. The experiments also show that the mean energy E_x increases as the pressure is reduced, and the probability of ionization in a collision increases with the energy of the electrons. The mean energy $E_{(x)}$, corresponding to the mean energy E_1 , may be found approximately by the following method:—

Let E_a be the mean energy of the electrons in the collisions with the atoms that are ionized when the gas is at the pressure p_a , so that one-half of the total ionization is due to electrons with energies greater than E_a . Let N_a be the number of electrons with energies greater than E_a in the space where the total number of electrons is N when the gas is at a pressure p less than p_a . The number of collisions with atoms in which the energy of the electrons exceeds the energy E_a is $N_a U_a p / L$ per second, where U_a is the mean velocity of the electrons with energies greater than E_a , and L the mean free path of an electron in the gas at 1 millimetre pressure. The energies of a very large proportion of these electrons are between the values E_a and $1.1 \times E_a$, so that the mean velocity U_a is about 2 per cent. greater than the velocity corresponding to the energy E_a .

If θ be the probability of ionization by collision when the velocity of the electron is U_a , the number of atoms that are ionized per second by electrons with energies greater than E_a is $\theta N_a U_a p / L$.

When the gas is at the pressure p_a this number is one-half of the total number that are ionized ($N \alpha w Z$) in the space where the total number of electrons is N .

The following equation is therefore obtained:

$$N \alpha w Z = 2 \theta N_a U_a p / L, \quad p = p_a, \quad . \quad . \quad . \quad (12)$$

or

$$\frac{\alpha}{p} = \frac{2 U_a \theta}{L w Z} \times \frac{N_a}{N}, \quad p = p_a. \quad . \quad . \quad . \quad (13)$$

8. If the pressure be reduced the number of electrons with energies near the value E_a is greatly increased, and the mean energy E_x of the electrons in the collisions with the atoms that are ionized is slightly greater than E_a .

More than half the total ionization is therefore due to collisions in which the energy of the electrons exceeds the value E_a . This is expressed by an equation similar to equation (12), with a numerical factor less than 2 in the expression on the right. If two-thirds of the total ionization were due to electrons with energies greater than E_a the numerical factor would be 1.5.

For a first approximation this factor may be taken as 1.5, and the quantities U_a and θ may be taken to be the same as in equation (13) when α/p is increased by lowering the pressure.

The corresponding value of the ratio N_a/N is then obtained from the following equation :

$$\frac{\alpha}{p} = 1.5 \times \frac{U_a \theta}{wZ \cdot L} \times \frac{N_a}{N}, \quad p < p_a. \quad . \quad . \quad (14)$$

9. As an example of the application of these formulæ E_a may be taken as the mean energy of the electrons in the ionization of atoms of helium when gas is at 12 millimetres pressure. In this case the mean energy of all the electrons is 3.5 volts, and the velocity wZ is 1.17×10^6 centimetres per second. Equation (13) thus reduces to

$$\frac{U_a \theta}{L} \times \frac{N_a}{N} = 186, \quad E_1 = 3.5, \quad p = 12 \text{ mm.} \quad . \quad (15)$$

When the pressure is reduced to 3 millimetres the mean energy of all the electrons is increased to 4.5 volts and the velocity wZ is 1.47×10^6 centimetres per second. The corresponding value of N_a/N as obtained from equation (14) is

$$\frac{U_a \theta}{L} \times \frac{N_a}{N} = 5120, \quad E_1 = 4.5, \quad p = 3 \text{ mm.} \quad . \quad (16)$$

The number N_a depends on the distribution of the energy about the mean energy E_1 , and it has been shown * that the ratio N_a/N may be expressed by an equation of the form

$$N_a/N = \phi(E_a/E_1).$$

The function ϕ has not been determined accurately, but an approximate formula for N_a/N in terms of E_a/E_1 has been found which may be used to find the energy E_a . This formula applies to cases where the distribution of the energies of the electrons is controlled by small losses of energy λE in collisions with atoms of the gas, λ being taken to be constant.

* Phil. Mag. ix. p. 1145 (June 1930).

Under these conditions the function ϕ is the same for all gases, and is independent of the pressure provided the electrons move in a uniform field of force so that the mean energy of agitation E_1 of the electrons is much greater than the mean energy of agitation of the molecules of the gas. Thus in equation (15) the ratio $N_a/N = \phi(E_a/3.5)$ and in equation (16) $N_a/N = \phi(E_a/4.5)$.

The following equation to determine E_a is obtained by eliminating the factor $U_a\theta/I_1$:

$$186 \phi(E_a/4.5) = 5120 \phi(E_a/3.5) \quad . \quad . \quad (17)$$

The solution of this equation, obtained from a table of values of $\phi(x)$, is $E_a = 11.7$ volts, and it represents the mean energy of agitation of the electrons in the collisions with atoms of helium that are ionized when the mean energy of agitation of all the electrons moving in a uniform electric field is 3.5 volts.

10. No serious error arises from the uncertainty of the value of the numerical factor on the right of equation (14), since a large error in this factor gives rise to a comparatively small error in the value of E_a . Thus if the factor were 1.75 instead of 1.5 E_a would be 11.2 instead of 11.7.

The maximum value of the numerical factor is 2 and the minimum is 1, the latter being the value when the pressure p is so much below the pressure p_a that nearly all the ionization is due to electrons moving with energies greater than E_a . In these cases the value of U_a and θ in equation (14) would be appreciably greater than in equation (13).

An upper limit to the value of E_a is obtained from these equations by taking the numerical factor on the right in equation (13) to 1 instead of 1.5. The value of E_a thus obtained is 12 instead of 11.7 volts.

The value of E_a in helium at 12 millimetres pressure may therefore be taken as 11.7 volts, and the probability θ of ionization in a collision when the energy of the electron is 11.7 volts is given by equation (15). In this case the ratio N_a/N is approximately 2×10^{-4} , which is the value corresponding to the ratio $E_a/E_1 = 3.34$. The mean velocity U_a is 2.1×10^8 centimetres per second, and the mean free path L is approximately .05 centimetre. The value of θ thus obtained is 2.3×10^{-4} .

The above value of the mean energy E_a is consistent with the results obtained in the investigation of the energies of the electrons that excite radiation in different parts of the spectrum. It was found that the mean energy of the electrons which excite the lines in the violet spectrum was

11.1 volts and the mean energy of the electrons which excite the red lines 10.5 volts when the mean energy of agitation was between 3.7 and 5.2 volts.

In neon at a pressure of 40 millimetres the mean energy of agitation is 4.3 volts, and the mean energy of the electrons in the collisions with atoms that are ionized is 13.5 volts. The probability θ of ionization in a collision by electrons with that amount of energy is 5×10^{-5} . The experiments on the measurement of the energies of the electrons that excite the lines in the different parts of the spectrum of neon are not yet completed, but the preliminary results are in agreement with this theory.

11. In these investigations no allowance has been made for the effect of losses of energy of the electrons in the collisions which excite radiation on the distribution of the energies about the mean energy of agitation E_1 . The number of these collisions is greater than the number in which the atoms are ionized, but it is uncertain to what extent they affect the coefficient of ionization corresponding to a given force and pressure.

If there were no losses of energy in large amounts except in the collisions where the atoms are ionized the supply of positive ions and electrons required to maintain the currents in the tubes would be obtained with forces smaller than those observed experimentally. If any correction were introduced to allow for losses of energy in the collisions which excite radiation the effect would be to diminish the values of the energies of the electrons in which the atoms are ionized, as calculated by this theory.

XCIV. *Some General Points of View with regard to the Rôle of the Solvent in the Electrolytic Dissociation of Salts.*
By FREDERICK KARL VICTOR KOCH, Ph.D., *Beit Scientific Research Fellow* *.

§ 1. *Electrolytic Dissociation and Solution Tension.*

THE factors determining the electrolytic dissociation of a salt in a given solvent (apart from concentration, temperature, etc.) are

- (1) The interionic forces.
- (2) The forces of ionic solvation.

* Communicated by Prof. James C. Philip, F.R.S.

If $(A_S)_C$ and $(A_S)_A$ are the respective free energies of transference of the cation and anion from a vacuum to the pure solvent, then

$$(A_S)_C = RT \cdot \log_e (a_S)_C,$$

$$(A_S)_A = RT \cdot \log_e (a_S)_A,$$

where $(a_S)_C$ and $(a_S)_A$ are the respective *solvation activities* (cf. Koch, Phil. Mag. (7) xi. p. 579 (1931)) ; and if $(A_M)_C$ and $(A_M)_A$ are the respective free energies of transference of the cation and anion from a vacuum to the salt, then

$$(A_M)_C = RT \cdot \log_e (a_M)_C,$$

$$(A_M)_A = RT \cdot \log_e (a_M)_A,$$

where $(a_M)_C$ and $(a_M)_A$ may be called the respective *salt activities*.

The ratios

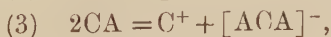
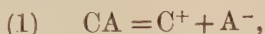
$$(a_S)_C / (a_M)_C = P_C,$$

$$(a_S)_A / (a_M)_A = P_A$$

are the respective distribution coefficients of the cation and anion between the solvent and the salt. These quantities, therefore, give a measure of the tendency of the ions to leave the salt and go into solution. P_C and P_A are similar to the Nernst solution tensions, but are, of course, not the same, since a_M is different* for the salt from what it is for the element electrode. P_C and P_A may, therefore, by way of distinction, be called the "*salt solution tensions*." The behaviour of each ion may thus be described in terms of its salt solution tension.

§ 2. Types of Electrolytic Dissociation.

The electrolytic dissociation of a salt, C_nA_m (where C is the cation and A is the anion) at a given concentration in a given solvent may be imagined to take place in a large number of ways. All these ways may, however, be placed in one or more of *four* categories. For example, for the uni-univalent salt CA :



* This difference was overlooked by Bodländer (*Z. Physikal. Chem.* xxvii. p. 55, 1898), who attempted to correlate the electrolytic dissociation and solubility of a salt with the solution tensions of its ions, as deduced from the element electrodes.

The general equations for a salt, C_nA_m are :

$$(1) \quad C_nA_m = n.C^+ + m.A^-,$$

$$(2) \quad C_nA_m = (n-x)[CA_{x/(n-x)}]^+ + (m-x)[AC_{x/(m-x)}]^- ,$$

$$(3) \quad C_nA_m = (n-x).C^+ + m[AC_{x/m}]^- ,$$

$$(4) \quad C_nA_m = n[CA_{x/n}]^+ + (m-x).A^- .$$

The following terminology is suggested :—

- (1) Simple symmetrical dissociation.
- (2) Complex ,, ,,
- (3) A-unsymmetrical ,,
- (4) C- ,, ,,

The last three categories may be grouped together under the term "*autocomplex dissociation*", corresponding to the term (already in use) "*autocomplex formation*". It is evident that autocomplex dissociation will pass over into simple symmetrical dissociation at very small concentrations of salt.

If every cation is not similarly situated to every other cation, or if every anion is not similarly situated to every other anion in the salt, then it is evident that certain groups of ions will be particularly stable. Under these conditions the dissociation must be autocomplex, and this may be regarded as a property of the salt alone. The concentration of the autocomplex ion may, however, be greatly influenced by the solvent. Thus, if the autocomplex ion is very stable, it will occur in all solvents; whilst if it is not very stable it will appear (in appreciable quantities) in some solvents but not in others. On this basis it would seem possible to be able to predict the kind of autocomplex ion from a knowledge of crystal structure. It must, however, be noted that the autocomplex formation which may thus be expected may be entirely masked by that induced by the solvent (see next paragraph), and further, that in the case of molecules consisting of more than two ions, when one ion has left the molecule the attractive force between those remaining will be increased, thus tending to produce an autocomplex ion.

If every cation is similarly situated to every other cation, and if every anion is similarly situated to every other anion in the salt, then P_C will be the same for all the cations and P_A will be the same for all the anions. The conditions

That autocomplex dissociation takes place in a large number of cases is shown from conductivity and transport-number data (see Jaques, 'Complex Ions in Aqueous Solution,' 1914; Walden, 'Elektrochemie Nichtwässriger Lösungen,' 1924). It should, however, be noted that transport-number data will not reveal the existence of complex symmetrical dissociation.

It seems reasonable to suppose that in the case of salts such as cadmium iodide, cobalt chloride, etc., which apparently always behave in an "anomalous" manner, the autocomplex dissociation is, in the main, a property of the salt.

An interesting case of A-unsymmetrical dissociation induced by the solvent is that of silver nitrate in pyridine. The solution tension of silver in pyridine has been found to be about 500,000 times greater than in water, whilst the solubility of silver nitrate in pyridine is only about one-tenth of that in water (Koch, J. Chem. Soc. 1928, p. 279). It therefore appears probable that P_{Ag^+} is much greater than $P_{NO_3^-}$ in pyridine. The existence of the ion $Ag(NO_3)_2^-$ in pyridine has been deduced from transport-number data by Abegg and Neustadt (*Z. physikal. Chem.* lxi. p. 486, 1909), whereas its presence in water under the same conditions has not been recorded.

It is not possible, in the present state of our knowledge, to state with certainty, in any actual case, to which of the several possible causes the particular type of dissociation must be attributed. Since, however, the probability of the condition $P_C = P_A$ holding exactly in any actual case is very small, it may be reasonably concluded that *electrolytic dissociation is, in general, unsymmetrical* (types (3) and (4)). The confirmation of formulæ (*e. g.* the Ostwald dilution law; the Debye-Hückel-Onsager theory of strong electrolytes) based upon the assumption of simple symmetrical dissociation may be attributed to the fact that investigations to test these formulæ are almost always carried out in dilute solution.

§ 3. *Electrolytic Dissociation and Dielectric Constant.*

The attractive force F between two *rigid* ions (having charges e_1 and e_2) at a distance x apart, in a *continuous* medium of dielectric constant ϵ , is given by Coulomb's law as

$$F = \frac{e_1 \cdot e_2}{\epsilon \cdot x^2}.$$

Thus, if two ions be imagined *as already separated*, then the force between them will decrease with increase in dielectric constant of the solvent. On this basis Nernst (*Z. physical. Chem.* xiii. p. 531, 1894) and Thomson (*Phil. Mag.* (5) xxxvi. p. 320, 1893) concluded that the electrolytic dissociation constant of a given salt should be greatest in that solvent which has the greatest dielectric constant. This point of view does not, however, explain how the ions were separated in the first place (*cf.* Fajans, *Naturwissenschaften*, ix. p. 736, 1921), and for this purpose it is *necessary* to postulate that the solvent molecules exert an attractive force on the ions. According to the Nernst-Thomson rule, this ionic-molecular force should increase with increase in dielectric constant of the solvent.

The solution tension of an ion, corresponding to the transference of the ion from the element electrode or a salt to a solvent, gives a measure of the attractive forces exerted by the solvent molecules upon that ion. Now it has been found (*cf.* Koch, *Phil. Mag.* (7) xi. p. 579, 1931) that the dielectric constant is not the only property of the solvent of which the solution tension is a function, but that it depends in general upon specific ionic-molecular forces. It therefore follows that *the electrolytic dissociation constant must also, in general, depend upon specific ionic-molecular forces.*

The following two formulæ correlating the dissociation constant with the dielectric constant of the solvent may, however, be mentioned.

Formula 1.—The free energy of dissociation (A_K) of a molecule in a given solvent may be split up into three parts: (1) the free energy of transference (A_μ) of the molecule from the pure solvent to a vacuum; (2) the free energy of dissociation (A_D) of the molecule into its constituent ions in the vacuum; and (3) the sum of the free energies of transference (ΣA_S) of the constituent ions from the vacuum to the pure solvent. Thus

$$A_K = A_\mu + A_D + \Sigma A_S.$$

If it be *assumed* (1) that the electronic configurations of the molecule and the ions are *rigid*, and (2) that the solvent is a *continuous* dielectric medium, then the free energy A_S is given by a calculation of Born (*Z. Physik*, i. p. 45, 1920) as

$$A_S = \frac{z^2 e^2 N}{2r} \left(1 - \frac{1}{\epsilon} \right),$$

and the free energy A_μ by a similar calculation of Martin (Phil. Mag. viii. p. 550, 1929) as

$$A_\mu = \frac{\mu^2 N}{3a^3} \left(1 - \frac{1}{\epsilon}\right).$$

In these expressions z is the valency and r is the radius of the ion, a is the radius of the molecule *assumed* to be a *rigid sphere* with a *small dipole*, μ , *at its centre*, ϵ is the dielectric constant, and N is the Avagadro number.

Born and Heisenberg (*Z. Physik*, xxiii. p. 388, 1924) have also calculated the free energy A_D for some simple cases theoretically, but since this free energy is independent of the solvent, it may, for the present purpose, be regarded as a constant.

It therefore follows that for a given salt

$$A_K = a' + b'/\epsilon,$$

where a' and b' are constants characteristic of the salt and independent of the solvent.

Now by the van t'Hoff isotherm,

$$A_K = RT \cdot \log_e K,$$

where K is the dissociation constant.

Hence, at any given temperature,

$$\log K = a + b/\epsilon,$$

where a and b are isothermal constants.

Since the basic conditions of this last formula (which, so far as the author is aware, has not been deduced previously) cannot reasonably be expected to be fulfilled in *natural cases*, the formula must be regarded only as representing an *ideal state*. There appears, unfortunately, to be a lack of data which would be sufficiently certain to give an adequate test of the extent of the validity of the formula.

Formula 2.—The Walden formula (*loc. cit.* p. 355) states that the dissociation constant should be proportional to the cube of the dielectric constant of the solvent, viz.,

$$K = c_W \cdot \epsilon^3,$$

where c_W is an isothermal constant characteristic of the salt and independent of the solvent.

The Walden formula appears to have received a fair amount of experimental confirmation (see Walden's book, *loc. cit.*).

It seems, however, to the author that the fact that this confirmation has been found is mainly due to the selection of substances with unusually simple properties (*e. g.*, Walden's "normal electrolyte" $(C_2H_5)_4N.I$) for investigation, and in general to undue allowances made for the uncertainty and inaccuracy of the values of the dissociation constants and dielectric constants.

§ 4. *Electrolytic Dissociation and Solubility.*

The factors determining the solubility of a salt in a given solvent (apart from temperature, etc.) are

- (1) The interionic forces.
- (2) The forces of ionic solvation.
- (3) The forces of molecular solvation.

Although it is sometimes found that there is a rough parallelism between the electrolytic dissociation constant and solubility, the additional factor (3), as also the fact that the solubility of autocomplex ions (if any) must be taken into account, shows that the appearance of this parallelism must be regarded as exceptional. Similarly, the parallelism which is sometimes found between the solubility of a salt and the dielectric constant of the solvent must also be regarded as exceptional (see § 3).

The solubility of a salt (as of a substance composed of neutral molecules) *will depend, in general, upon specific forces of solvation.* It is clear that the solubility (as the electrolytic dissociation constant) must ultimately be calculable in terms of the electric and magnetic properties of the solute and solvent. Our present knowledge of these properties and of the manner in which such knowledge would have to be applied is, however, so meagre that a further discussion, *from the general standpoint*, would be premature.

In conclusion, the author wishes to express his indebtedness to the Trustees of the Beit Fellowship for a Fellowship.

Physical Chemistry Department,
Imperial College of Science and Technology,
London, S.W.7.

XCV. *A Note on White Dwarfs and the Limiting Density of Matter.* By D. S. KOTHARI, M.Sc.*

§ 1.

IN the white dwarfs matter reaches a density of the order of 10^5 gm./cm.³, and this is possible, for the atoms in these dense stars have reached their last stages of ionization and mostly exist as bare nuclei and free electrons. The subject has been discussed by several authors⁽¹⁾. Stoner and Frenkel consider the star as a mass of uniform density, and determine the equilibrium condition by the variation

$$\frac{d}{dn}(E_k + E_g) = 0,$$

where E_k is the kinetic energy of the electrons, E_g the gravitational energy of the star, and n the number of electrons in unit volume. Chandrasekhar⁽¹⁾ proceeds by the method of polytropes, but, as these different procedures lead only to trivial changes in the numerical values of the final formula, Stoner's method alone is followed here.

Stoner obtains

$$M = 1.751 \times 10^{34} [F(x)]^{3/2}, \quad . \quad . \quad . \quad (1)$$

where

$$F(x) = \frac{1}{8x^3} \left[\frac{3}{x} \log \{x + (1 + x^2)^{1/2}\} + (1 + x^2)^{1/2} (2x^2 - 3) \right] \quad (2)$$

and

$$x = \frac{p_0}{m_0 c} = \frac{1}{m_0 c} \left(\frac{3h^3 n}{8\pi} \right)^{1/3} \quad . \quad . \quad . \quad (3)$$

When $x \rightarrow \infty$, M becomes

$$1.751 \times 10^{34} \left(\frac{1}{4}\right)^{3/2} = M_0,$$

$$\log M_0 = 33.3401.$$

If the star has a mass $M < M_0$, it has an equilibrium configuration of finite density (ρ) determined by (1); but if $M > M_0$, the star has no equilibrium configuration and $\rho \rightarrow \infty$.

* Communicated by the Author.

§ 2.

It is obvious that ρ could not increase above a certain maximum value ρ_0 . The order of ρ_0 may be comparable to 10^{13} gm./cm.³, for n could be of the order of 10^{39} , as the electrons and nuclei have radii of the order of 10^{-13} cm.

Let us suppose that α is the volume that is excluded by each electron for interaction with other electrons. α has the same significance for the electron as the b term in Van der Waal's equation has for the atom. When we take into account this fact of excluded volumes, it is easily shown that*

$$E_K = \frac{8\pi V m_0^4 c^5}{h^3} (1 - n\alpha) \left[\frac{1}{8} x(1 + x^2)^{1/2} (1 + 2x^2) - \frac{x^3}{3} - \log \{x + (1 + x^2)^{1/2}\} \right], \quad (4)$$

$$x = \left(\frac{3h^3 n}{8\pi} \right)^{1/3} \frac{1}{m_0 c (1 - n\alpha)^{1/3}} = \frac{x_0}{(1 - n\alpha)^{1/3}}, \quad \dots \quad (5)$$

where x_0 is the value of x when excluded volumes are neglected.

When

$$x \ll 1, \quad E_K = N \frac{3}{40} \left(\frac{3}{\pi} \right)^{2/3} \frac{h^2}{m_0} \left(\frac{n}{1 - n\alpha} \right)^{2/3}, \quad \dots \quad (6)$$

$$x \gg 1, \quad E_K = N \frac{3}{8} \left(\frac{3}{\pi} \right)^{1/3} hc \left(\frac{n}{1 - n\alpha} \right)^{1/3}. \quad \dots \quad (7)$$

Again⁽²⁾,

$$E_G = -\frac{3}{5} GM^{5/3} (2.5 m_H)^{1/3} \left(\frac{4}{3} \pi n \right)^{1/3} \dots \quad (8)$$

$$= 3^{1/3} \left(\frac{4\pi}{5} \right)^{2/3} \frac{GM^{5/3} m_H^{1/3} m_0 c}{h} (1 - n\alpha)^{1/3} x, \quad (9)$$

$$E_K = \frac{3M m_0 c^2}{2.5 \cdot m_H} \frac{f_1(x)}{x^3}, \quad \dots \quad (10)$$

$$f_1(x) = \left[\frac{1}{8} x(1 + x^2)^{1/2} (1 + 2x^2) - \frac{x^3}{3} - \log \{x + (1 + x^2)^{1/2}\} \right].$$

* A rigorous derivation of this, when excluded volumes are taken into account, will be shortly published in another paper containing a detailed discussion of the dissociation theorem from statistical mechanics.

Applying the variation

$$\frac{d}{dx} (E_K + E_G) = 0,$$

we obtain

$$F(x) = 1.483 \times 10^{-23} M^{2/3} (1 - n\alpha)^{4/3},$$

$$M = 1.751 \frac{[F(x)]^{3/2}}{(1 - n\alpha)^2} \dots \dots \dots (11)$$

Our result thus shows that there is an equilibrium configuration possible for every value of M, and that the maximum density corresponding to $n=1/\alpha$ is attained only when $M \rightarrow \infty$.

When $x \gg 1$, we have the approximation

$$r = 1 - \sqrt{\frac{M_0}{M}}, \dots \dots \dots (12)$$

where r is the ratio of the actual density for the star of mass M to the maximum density possible for matter. For $M=10M_0$ we have $r=0.68$.

When $x \ll 1$, we have $\rho \ll \rho_0$ and

$$q = (1 - \rho/\rho_0)^{5/2},$$

where q is the ratio of the actual density of the star (ρ) to what it would be for a star of mass M , but without taking the excluded volumes into account.

§ 3.

The conception of excluded volumes also enables us to see the reason for the complete ionization of the atoms in the white dwarfs. If a nucleus captured an electron and formed an atom, the atom formed will exclude for the free electrons a volume equal to a^3 , where a is comparable to the radius of the atom formed. Thus, when the atom is formed there becomes available the energy initially possessed by the electron before its capture by the nucleus (the atom formed being non-degenerate, possesses negligible energy), but if this energy is insufficient to balance the increase in the kinetic energy of the degenerate electron gas due to the diminution in its volume by a^3 , no atom formation can take place, *i. e.*, the state will be one of complete ionization.

Hence we obtain, from the equation for E_K given before,

$$\left. \begin{aligned} n &\geq \frac{5}{2a^3} & x < 1, \\ &\geq \frac{4}{a^3} & x > 1. \end{aligned} \right\} \dots \dots (13)$$

This relation puts a lower limit on n (*i. e.*, ρ), and it certainly predicts values of the correct order of magnitude.

$$a = \frac{\alpha_{\text{Hydrogen}}}{Z}, \text{ approximately,}$$

Z the atomic number;

$$\therefore n > \frac{5}{2} \cdot \frac{Z^3}{a_H^3} > \frac{(10)^3}{a_H^3} > 10^{27},$$

taking $Z=10$ on the average.

Equations of § 2 show that for any star of mass M there is a definite maximum density that it can attain, and equation (13) puts a definite lower limit on the density of the stars of the white dwarf type. The actually observed densities lie near this lower limit. It would not be of much use in the present state to make complete numerical computations, and so only the orders of magnitude are indicated here.

Summary.

1. In determining the equilibrium configuration the idea of "excluded volumes" is introduced, and hence it is shown that there is an equilibrium configuration for every mass M of the dense star.

2. The cause of complete ionization in the white dwarfs is discussed, and it is shown that for such stars there should exist a certain minimum limiting density.

References.

- (1) Frenkel, *Zs. f. Phys.* l. p. 234 (1928); Stoner, *Phil. Mag.* ix. p. 944 (1930); Milne, *M. N. R. A. S.* xci. (1931); Chandrasekhar, *Phil. Mag.*, Feb. Suppl. 1931, p. 592; Majumdar and Kothari, *Zs. f. Phys.* lxi. p. 712 (1930).
- (2) Stoner, *Phil. Mag.* ix. p. 949 (1930).

Belvior Road, Cambridge.
March 1931.

XCVI. *Notices respecting New Books.*

National Physical Laboratory—Collected Researches. Vol. xxii. 1930. (His Majesty's Stationery Office. Price £1 net.)

OF the twenty-one papers in this collection of reasearches, a considerable proportion have appeared during the last four or five years in the pages of the 'Journal of the Institute of Electrical Engineers' and deal largely with problems undertaken in the programme of the Radio Research Board, fourteen papers in all. Mr. Wilmotte's name appears in connexion with seven of these papers, theoretical and experimental researches on receiving and transmitting antennæ, the directivity of beam systems, condenser losses at radio frequencies, and the construction of a standard high-frequency inductive resistance. The experimental measurement of the natural wave-length of a simple antenna agrees with the theoretical value given by Abraham and Föppl. Other papers deal with the theory of receiving aerials, the measurement of condenser resistance and anode circuit impedances, the performance of amplifiers, and the production of small known voltages and currents at radio frequencies. Mr. Vigoureux contributes two papers on the quartz oscillator, the first showing how the inductance and capacity of the equivalent electrical circuit can be expressed in terms of the elastic and piezoelectric constants, and the second, giving a theoretical discussion of the behaviour of a valve maintained quartz oscillator: Dr. Hartshorn on the determination of dielectric constants and Dr. Rayner on the design and use of an air-condenser for high voltages. The remaining papers describe the experimental work carried out on sheath losses in single conductor lead-covered cables, the impedances of three phase-line cables and their comparison with the values calculated from formulæ, current rating of low tension cables, current capacity of copper and aluminium bus bars and other related problems.

Standard four-figure Mathematical Tables. By L. N. MILNE-THOMSON, M.A., and L. T. COMRIE, M.A., Ph.D. (Macmillan & Co. Price 10s. 6d.)

BOTH Dr. Comrie and Prof. Milne-Thomson, to reverse the order of their names, have recently published mathematical tables, the former, a second and completely revised edition of Barlow's tables, the latter, a table of square roots. In collaboration, they have produced a very complete and accurate set of four-figure tables of trigonometric, hyperbolic, and other functions. Tables of $\tan x$, $\sec x$, $\coth x$, the inverse trigonometric and hyperbolic and other functions were computed specially for this volume from first or

second differences. The larger tables include natural and logarithmic trigonometrical functions in degrees and decimal parts of a degree, as in the ten-figure tables of Peters, arranged in ten columns: the same functions in degrees and minutes for each minute of angle: in radians for the first quadrant by intervals of 0.001 radian and as far as 7.9 radians by 0.1 radian: the hyperbolic functions, with their logarithms and exponential powers over varying ranges of the argument as far as 15.0; and an extensive set of tables of inverse functions as well as tables of roots, powers, and reciprocals on the lines of Barlow. Among the shorter tables included in the collection are the Gudermannian and its inverse, the gamma and error functions, and addition and subtraction logarithms. A very important and useful feature of this volume is the introduction of critical tables of second difference coefficients and of the auxiliary functions S, T, Sh, and Th, and the employment of high dot and low dot to indicate approximately the value of the fifth decimal place: with this device, the tables might be described as four-and-a-half place tables: the colon has long been used to represent half a unit in the last place of decimals.

Of the two editions, one gives positive and the other negative characteristics in the entries of logarithms. The book is beautifully printed and arranged; compared with some mathematical tables which have recently appeared on the Continent, the price of the Standard four-figure tables is very reasonable and brings it within the reach of all who require the constant use of tables to four decimals.

Tables Annuelles de Constantes et Données numériques.

Vol. vii. in two parts, 1925-6.

Tables des Matières des Volumes I.-V. 1910-1922.

(Gauthier-Villars et Cie, 55 Quai des Grands-Augustins, Paris.

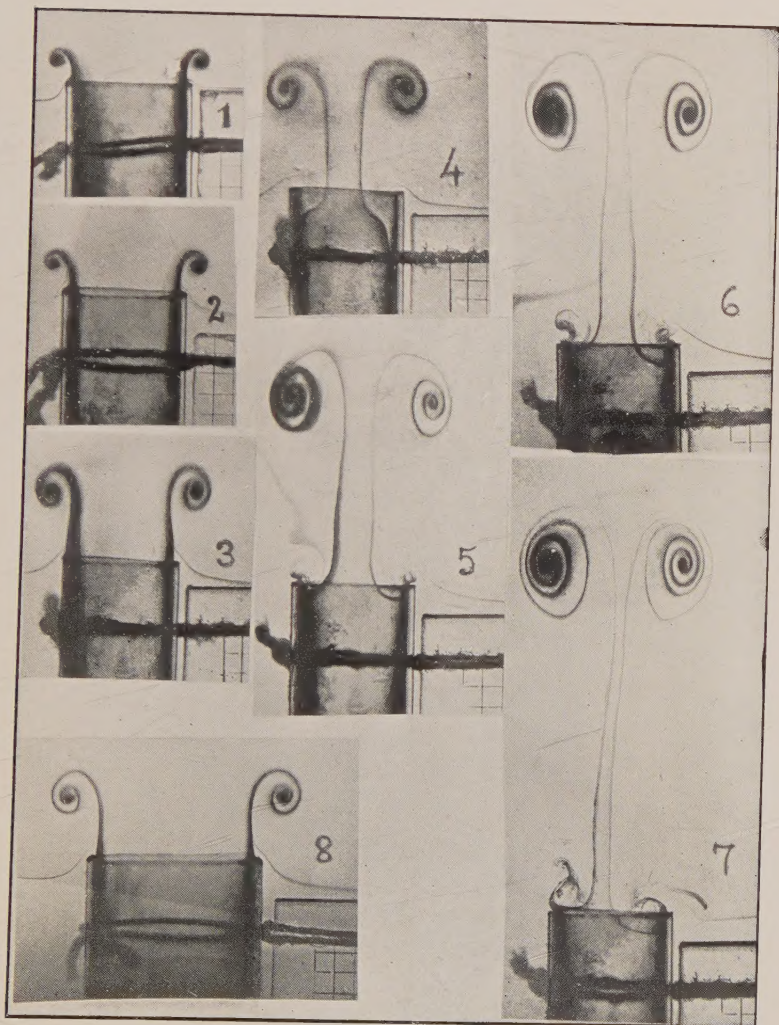
McGraw-Hill Book Company, 370 Seventh Avenue, New York.)

THE seventh volume of the Tables of Constants and Numerical data, like its predecessors, affords remarkable evidence of the progress made during recent years in the domain of physics, chemistry, biology, and engineering. In particular, solubilities, vapour pressures, thermodynamics, electrolytes, emission and absorption spectra are treated very fully in this volume, other chapters dealing with the experimental results on surface tension, viscosity, chemical equilibrium and velocity of reaction, colloids, adsorption, as well as biological and engineering researches. Many of the sections are preceded by explanatory notes giving details of notation, abbreviations and definitions, and the use of the tables, with extensive bibliographies of the memoirs published during the period under review. The various branches of research have been under the charge of specialists, and some hundreds of scientific journals have been consulted in the compilation of this volume:

much material, otherwise inaccessible, is here made available for research workers generally. In addition to the sections which have appeared in earlier volumes, two new chapters on explosives and explosions in gaseous mixtures have been introduced, whilst other chapters on absorption spectra, dielectric constants, and X-ray analysis indicate the extent of the researches since the appearance of the sixth volume. Dr. Brüninghaus has edited the long section on emission spectra of elements and their hydrides, oxides, and other compounds. Prof. V. Henri's work on the quantitative analysis of absorption spectra, commenced twenty years ago, has been developed at a great rate by the introduction of new and improved methods of measurement. He has brought about a unification of the diverse results published during the last few years, has revised the graphical data and plotted the results on a uniform scale: absorption curves for more than three hundred substances are given, including aniline and its derivatives and the alkaloids. The more important sections of the volume, *e. g.*, spectra, electricity and magnetism, crystallography, colloids, etc., are issued in separate parts for the convenience of workers whose interests are confined to these particular branches of scientific research. Information with regard to the reduced subscription rates for the present year may be obtained on application to Dr. Charles Marie, 9 rue de Bagneux, Paris.

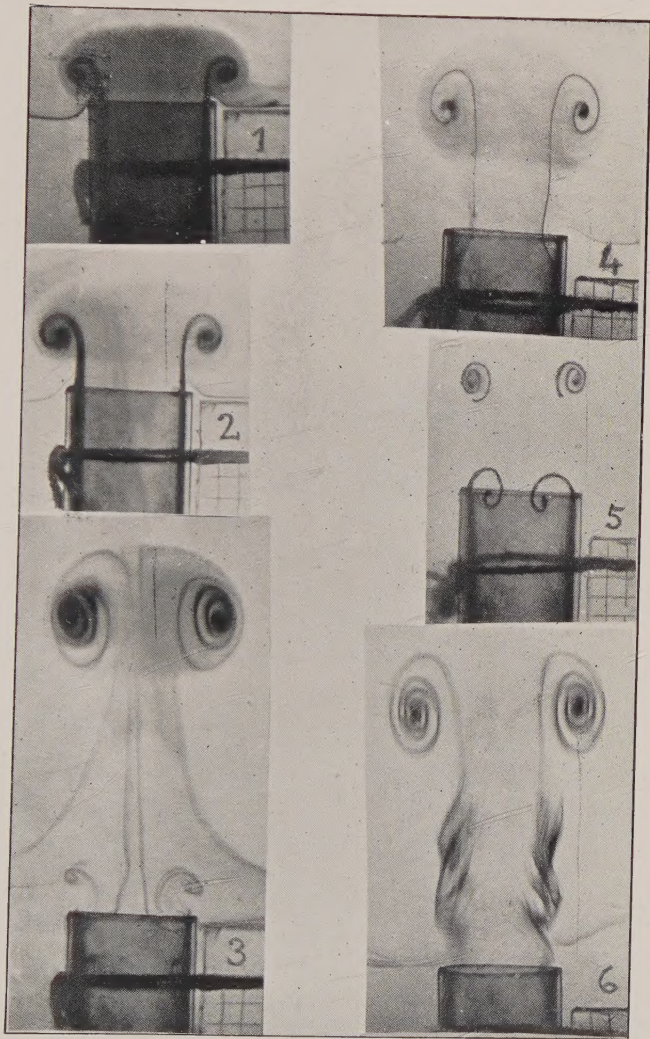
The Index to the first five volumes of this series of Annual Tables of Constants provides a ready and convenient means of ascertaining the development of physical, chemical, and other researches during the twelve or thirteen years to the end of 1922. Of the three parts into which the index is divided, the first gives an analysis of the numerous tables given in the earlier volumes of the series, with references to the particular chapter and volume; the second, an alphabetical arrangement of all substances which have been the subject of investigation during that period; and the last, a very complete index of formulæ. The magnitude of this undertaking may be judged by the fact that references are given to more than twenty thousand substances. Dr. Kravtsoff is to be congratulated on the completion of his arduous and laborious task and the publishers on the production of an encyclopædic work of reference which will be invaluable to scientific workers.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]



Illustrating development and mechanism of spiral vortices.

Figs. 1-7. Diam. of tube 1.5 cm, liquid ejected 6 c.c. at pressure 14 cm.
 Fig. 8. Diam. of tube 2.1 cm., liquid ejected 12 c.c. at pressure 14 cm.



Illustrating development and mechanism of spiral vortices. (Diameter of tube 1.5 cm.)

Figs. 1-3. Shows movement of front and associated development of spirals; liquid ejected 6 c.c. at pressure 14 cm.

Fig. 4. Liquid ejected 6 c.c. at pressure 24 cm.

Fig. 5. Liquid ejected 1.5 c.c. at pressure 14 cm. Shows a counter-vortex near mouth of tube. (Retouched.)

Fig. 6. Liquid ejected 12 c.c. at pressure 14 cm. Shows turbulent tail, ...

